

ALKYL CHAIN ORDER AND MOBILITY IN SOME IONIC AND NONIONIC SURFACTANT SYSTEMS

A nuclear magnetic
resonance study



JOHN THOMAS AHLNÄS

1985

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Abstract Nuclear Magnetic Resonance (NMR) methods are used to study some ionic and nonionic surfactant systems. For the first time order parameters of alkyl chains in surfactant aggregates have been determined from field dependent ^{13}C -NMR spin-lattice relaxation. In addition to the order parameters, fast motion correlation times along the surfactant alkyl chain were determined. A slow motion correlation time was present in all aggregated systems studied here. For sodium octanoate and sodium dodecyl sulfate micelles the slow motion was consistent with the aggregate tumbling and monomer lateral diffusion on the aggregate surface. Order parameter profiles are shown to vary within and between various phases. Experimental order parameters agree with theoretically calculated from the single chain model. Complexes of the molar ratio 2 octanoic acids to 1 sodium octanoate are formed in this binary solution. High order parameters close to the polar head was found. Self-diffusion measurements indicated that additional acid is hydrogen bonded to these complexes. This additional acid is not seen in ^{13}C -NMR chemical shifts since it is indistinguishable from octanoic acid dimers. For penta ethylene oxide dodecyl ether in water and as neat liquid frequency dependent relaxation was found. ^{13}C shifts indicated increased amount of gauche conformations at lower temperature for the ethoxide chain. These and other experimental results supports a recent theory for ethoxide chains.			
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Date July 8, 1985

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LIST OF PAPERS

The thesis presented here consists of a summary and the following papers:

- I. CARBON - 13 NUCLEAR MAGNETIC RESONANCE RELAXATION IN MICROEMULSIONS. AGGREGATION IN THE EXTENSIVE SOLUTION PHASE OF SODIUM OCTANOATE - OCTANOIC ACID - WATER SYSTEM.

T. Ahlmas, O. Soderman, C. Hjelm and B. Lindman,
J. Phys. Chem., 87(1983)822

- II. SURFACTANT ALKYL CHAIN MOBILITY AND ORDER IN MICELLES AND MICROEMULSIONS

T. Ahlmas, O. Soderman, H. Walderhaug and B. Lindman
"Surfactants in Solution", Eds. K. L. Mittal and
B. Lindman, vol. 1, p. 107, Plenum, New York (1984)

- III. AGGREGATION, HYDROCARBON-CHAIN ORDER AND MOBILITY IN THE SYSTEM OCTANOIC ACID - SODIUM OCTANOATE. A C-13 NMR CHEMICAL SHIFT, NUCLEAR OVERHAUSER ENHANCEMENT, SPIN-LATTICE RELAXATION AND H-1 - NMR SELF-DIFFUSION STUDY.

T. Ahlmas and O. Soderman, Colloids and Surfaces,
12(1984)125

- IV. SURFACTANT ALKYL CHAIN ORDER IN THE ISOTROPIC AND ANISOTROPIC PHASES OF THE SYSTEM SODIUM OCTANOATE - OCTANOIC ACID - WATER.

T.Ahlnas, O.Soderman and H.Walderhaug,
(to be published)

V. FOURIER TRANSFORM CARBON-13 RELAXATION AND SELF-
DIFFUSION STUDIES OF MICROEMULSIONS. (*)

B.Lindman, T.Ahlnas, O.Soderman, H.Walderhaug, K.Rapacki
and P.Stilbs, Faraday Discuss. Chem. Soc., 76 (1983) 317

VI. NONIONIC SURFACTANTS IN NEAT LIQUID AND MICELLAR
SOLUTION STUDIED BY C-13 NMR RELAXATION AND
CHEMICAL SHIFTS.

T.Ahlnas (to be published)

VII. A MULTIFIELD C-13 NMR RELAXATION AND NUCLEAR
OVERHAUSER ENHANCEMENT STUDY OF SODIUM DODECYL
SULFATE MICELLES.

T.Ahlnas and B.Lindman, (to be published)

*) C13-NMR part

1. INTRODUCTION

In this thesis nuclear magnetic resonance (NMR) is used to study the order and mobility of surfactants in various phases.

For the first time a new method of determining alkyl chain order and mobility in isotropic solutions of aggregated surfactants is presented. We have used frequency dependent spin-lattice relaxation (at three magnetic field strengths) to determine three parameters; a fast motion correlation time associated with the gauche-trans isomerism of the carbon-carbon bond, a slow motion correlation time associated with the aggregate tumbling and the lateral diffusion of monomers at the aggregate surface and a order parameter describing the anisotropy of the fast local motions. We have used this method to investigate surfactant alkyl chain order and mobility in both ionic and nonionic surfactant systems. Order parameters extracted from field dependent C13 relaxation in isotropic phases have been compared to order parameters determined from deuterium NMR quadrupolar splittings in anisotropic phases. Also, a comparison of experimentally and theoretically determined order parameters has been done.

Nuclear magnetic resonance methods have since ca. 1970 been used to investigate surfactant systems. Chemical shifts, relaxation, line-shapes, quadrupolar splittings and self-diffusion have been the main areas of interest. Still, as the theory and experimental techniques continue to

develope, NMR will provide novel information on surfactant systems.

1.1 SURFACTANTS (1- 4)

1.1.1 Structural Features

Surfactants are molecules with a polar (hydrophilic) part and a nonpolar (hydrophobic, usually a alkyl chain) part. In water the nonpolar part avoids water contact while the polar part readily is in contact with water. In order to satisfy these desires surfactants aggregate in water and adsorb to surfaces.

Surfactants are devided into groups according to the nature of their polar part.

anionic: like sodium octanoate

cationic: like cetyl tri methyl ammonium bromide

nonionic: like penta ethylene oxide dodecyl ether

zwitterionic: like 2-octyldimethylammonioethyl sulfate

When immersed in water surfactants can form a variety of aggregate structures like micelles (in the L1-phase), inverted micelles (in the L2-phase), rods (in the L1 and E-phase), inverted rods (in the F-phase) and lamellae (in the D-phase).

An example of these structures is given in the phase diagram (fig. 1).

1.1.2 Surfactant Applications

Surfactants are used in many areas of everyday life, for instance as detergents and cleaners, in foods, paints, textiles, paper, cosmetics, flotation of minerals, drugs, in oil recovery, as plant protection and pesticides, etc. From these examples, it is also evident that surface and colloid chemistry is more important in many areas than usually is recognized.

2. NUCLEAR MAGNETIC RESONANCE (5-7)

2.1 Some Basic Principles

Most atomic nuclei, or an isotope of them, possess a spin and a magnetic moment. This magnetic moment will interact with strong magnetic fields. The spin is quantized and for C^{13} we have two allowed spin states. When placed in a strong magnetic field the two states will be unequally populated. The population difference will increase with increasing magnetic field strength and with decreasing temperature.

Since, there is an energy difference between the two states, we will be able to induce transitions by applying an oscillating magnetic field at the resonance frequency. Sweeping the field or the frequency will enable signal detection. In modern NMR instruments r.f. pulses and Fourier transformation are used.

This is the basic principle of attaining a NMR signal

Until now, we have just discussed the interaction between one nucleus and a magnetic field. In real systems, like a surfactant molecule, the C^{13} nuclei in the alkyl chain interact with each other and directly attached protons. However, the low (1.1%) abundance of the C^{13} isotope ensures negligible contribution from C^{13} - C^{13} interactions. The dipole-dipole interaction between the carbon and the proton provides a mechanism for mediating extra energy (from pulsing) of the spin system (CH_2 or CH_3 group) to the environment. This is called spin-lattice relaxation and the time constant for this process is denoted T_1 . Physically, this can be followed in an inversion recovery experiment (see fig.2.) as the change in signal intensity.

In addition to the above process there is a mechanism for reaching equilibrium within the spin system. This process is called spin-spin relaxation and the characteristic time constant is T_2 . T_2 can be determined from the signal linewidth.

2.2 Spin-lattice Relaxation

When the spin system is not at equilibrium with the lattice, energy is transferred through random interactions (fluctuations) until equilibrium is reached. The relaxation process may usually be described (for Brownian systems) by an exponentially decaying (time dependent) correlation function. The characteristic time (T_1) for the spin-lattice relaxation process is related to the ensemble averaged

transition probabilities which in turn are given by the Fourier transform of the correlation function. This correlation function contains information on the molecular motions. The Fourier transformation of the time dependent correlation function gives a spectral density function.

For simple liquids the relaxation time T_1 (at extreme narrowing conditions) is given by

$$\frac{1}{T_1} = \left[\frac{\mu_0 \hbar \gamma_C \gamma_H}{4\pi r_{C-H}^3} \right]^2 \cdot N \cdot \tau_c \quad (1)$$

where τ_c is the correlation for the motion causing relaxation, N is the number of directly bond protons, r is the carbon-proton distance and the other symboles have their usual meaning.

2.2.1 Spin-lattice Relaxation in Surfactant Systems(8)

In surfactant systems the correlation function is not describable by a single correlation time. The reason is that experimentally we observe a relaxation time that would imply so called "extreme narrowing" conditions and still, we find frequency dependent relaxation.

From these observations Wennerstrom et al.(8) formulated the so called "two-step" relaxation model. In this model the total correlation function consists of two correlation functions, one for the fast motions and one for slow motions. The fast motions are slightly anisotropic and the slow motions are isotropic. Thus, this model takes care of prior knowledge of of micellar systems, that is, anisotropic and the fast local motions in the alkyl chain in

liquid crystalline phases, aggregation and thereby a slow isotropic motion of the aggregate and lateral diffusion of monomers on the aggregate surface. The anisotropy is evidenced by the splittings in deuterium spectra of per-deuterated surfactants in liquid crystalline phases. The liquid like alkyl chains are evidenced by the diffuse X-ray band at 4.5 Å.

The spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = \left[\frac{\mu_0 \gamma_C \gamma_H}{4\pi r_{C-H}^3} \right]^2 \left\{ 2(1-S^2)\tau_c^f + S^2 \frac{1}{5} \left[\frac{3\tau_c^s}{1 + \omega_C^2 \tau_c^s{}^2} + \frac{\tau_c^s}{1 + (\omega_H - \omega_C)^2 \tau_c^s{}^2} + \frac{6\tau_c^s}{1 + (\omega_H + \omega_C)^2 \tau_c^s{}^2} \right] \right\} \quad (2)$$

where τ_c^f and τ_c^s are the correlation times for the fast and slow motions, ω_C and ω_H are the resonance frequencies in units of radians per second, S is the local order parameter defined as the time average

$$S = \frac{1}{2} \langle (3 \cos^2 \theta_{MD} - 1) \rangle \quad (3)$$

θ_{MD} is the angle between the local symmetry director and the C-H bond. The average is taken over a time long enough to average the fast local motion. Further, it is assumed that the fast motions have a three fold or higher symmetry around the local director. For all aggregate structures studied here the local symmetry director is assumed to coincide with the molecular axis and to be perpendicular to the aggregate surface. The only exceptions are the hexagonal and inverted hexagonal structures where the local symmetry director is parallel to the aggregate long axis. The field and slow motion correlation time dependence of equation (2) is shown in fig. 3.

3. SUMMARY OF THE MOST IMPORTANT RESULTS

In this section we will discuss our experimental observations and the conclusions we have drawn.

3.1. Micellar L1 Phases

In papers II, VI and VII micellar phases of sodium octanoate(NaC8) - water, penta ethylene oxide dodecyl ether(C12E5) - water and sodium dodecyl sulfate(SDS) - water, respectively are studied. In all cases frequency dependent relaxation is observed. Below the critical micelle concentration (CMC) no frequency dependent relaxation was observed(II). If the CMC is high the contribution from the free monomers to the relaxation should be taken into account. For longer chain surfactants, like C12E5 and SDS, the relaxation rates ($1/T_1$) are weakly concentration dependent. In cases where nuclear Overhauser enhancement (n.O.e) was measured, significantly reduced values from full n.O.e were obtained for most of the carbons.

Analysis of the data by the "two-step" model gave good fits to the experimental data. Three parameters, the order parameter S, the fast motion correlation time and the slow motion correlation time, were obtained from the analysis.

The fast local motions are shown to be slightly anisotropic. The order is decreasing when going from the polar end to the terminal methyl. The order parameter values are between .25 and .02. For the nonionic C12E5

surfactant somewhat lower order was found when compared to ionic surfactants with equal alkyl chain length.

The fast local motion correlation times are in the 5 to 30 pico second range and slowest at the alkyl chain water interface. This supports the picture of a liquid-like interior of the micelle. For C12E5 some slower fast local motions than for SDS were obtained.

The slow motion (in the nano second range) is for NaC8 and SDS micelles shown to depend on the aggregate tumbling and the lateral diffusion of monomers on the aggregate surface. For C12E5 the slow correlation time was short compared to the expected motional correlation time from the aggregate size and the estimated lateral diffusion coefficient. Since the micellar aggregates (probably flexible rods)(9) are extended, further analysis of the slow motion correlation time was not done. It has been shown by Walderhaug et al.(10) that low field H₂-NMR relaxation should be used to properly characterize the slow motions in systems with extended aggregates.

3.2 The L2 Phases

In papers I (see also II and IV), III, V and VI we have studied the systems: sodium octanoate - octanoic acid - water, sodium octanoate - octanoic acid, sodium octyl benzene sulfonate - butanol - toluene - water, neat liquid tetra and penta ethylene oxide dodecyl ether.

In paper I a microemulsion model system and in paper V a microemulsion system is studied. Field dependent relaxation is observed as well as reduced n.O.e. The presence of a slow process indicates that some aggregate structure has to prevail at least on this time scale. In papers III and VI water free systems are studied. In the octanoic acid - sodium octanoate system field dependent relaxation and reduced n.O.e were found but not for pure octanoic acid. Complexes with the molar ratio 2/1 are formed in the octanoic acid - sodium octanoate system. Besides the C13 NMR chemical shifts and relaxation, the self-diffusion was studied. Self-diffusion coefficients indicated concentration dependence in the aggregation number. This was interpreted as hydrogen bonding of octanoic acid to the complex. Chemical shifts and IR cannot distinguish this state from the dimeric neat octanoic acid. The order parameter was quite high (.4) at the head group and decreased rapidly when going to the terminal methyl.

Neat liquid C12E4 and C12E5 are aggregated since frequency dependent relaxation was observed. The order parameters were some higher than in the micellar phase.

3.3 The Anisotropic Phases

In paper IV alkyl chain order parameters in the system sodium octanoate - octanoic acid - water were determined using H2-NMR quadrupolar splittings from per- and a-deuterated sodium octanoate.

The order parameter profile is different in the various phases and reflects the differences in the conformational freedom of the alkyl chains. The order parameter of the α -carbon was found to decrease as the water content was increased in the lamellar phase. Also, if the ratio octanoic acid to sodium octanoate was increased the order was found to decrease.

High resolution C^{13} NMR spectra of C12E5 in the lamellar and the hexagonal phases were observed. These slightly broadened signals are unexpected and they indicate that there are some slow motions that are quite fast and isotropic.

3.4 C^{13} Chemical Shifts of Nonionic Surfactants

In paper VI, C^{13} chemical shifts of C12E5 were measured as a function of temperature and concentration. It was concluded that in the ethoxide chain part the amount of gauche conformations was increased (contrary to what is found for the alkyl chain) when the temperature was decreased or if the environment was made more polar. These results strongly support a recent theory for nonionic surfactants(11). In this theory it is suggested that conformational equilibrium in the ethoxide chain segment varies with temperature and polarity of the environment. More gauche states were found at lower temperature or when the environment was made more polar. The change in the ethoxide chain gauche-trans equilibrium to more trans at higher temperatures was argued to cause phase separation at

cloud point. The reason would be at that temperature the more hydrophobic nature of the ethoxide chain.

3.5 General Conclusions

Field dependent relaxation as well as reduced n.O.e's were observed in all isotropic aggregated surfactant systems studied here.

In paper IV as well as papers II and VII order parameters are compared with other order parameters from either experiments or simulations. Good agreements were found between our experimental order parameters and those determined from single chain simulations.

The order parameter profiles are sensitive to aggregate form and more so for short chain surfactants. Minor differences in order parameter values were detected between ionic surfactants with equal chain length.

Fast motion correlation times are in the ps range and are slowest close to the polar head.

For small aggregates the slow motion is ascribed to the aggregate tumbling and lateral diffusion of the monomers.

For larger aggregates with unknown forms C13 relaxation is not alone capable of determining all slow motions.

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FIGURE CAPTION

Fig. 1. A schematic phase diagram of sodium octanoate, decanol and water with the aggregate structure in the various phases indicated.

Fig. 2. A inversion recovery experiment in the L2 phase of sodium octanoate, octanoic acid and water.

Fig. 3. The field and slow motion correlation time dependence of the 'two-step' spin-lattice relaxation model. The order parameter is set to .2 and the fast motion correlation time to 2×10^{-11} s.

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This far, my interest in surface and colloid science has brought me to several stimulating places. My curiosity was triggered while studying at Åbo Akademi in Finland, at the department of Physical Chemistry, headed by prof. Ingvar Danielsson. An eight month's period at the Swedish Institute of Surface Chemistry, headed by prof. Per Stenius, provided a very stimulating time and opened the breath taking view of surface and colloid science both considering the applications and the basic research. Then, it was not hard to decide when prof. Björn Lindman kindly invited me to continue the studies in Lund. As a matter of fact, the decision took me no time but to express it .

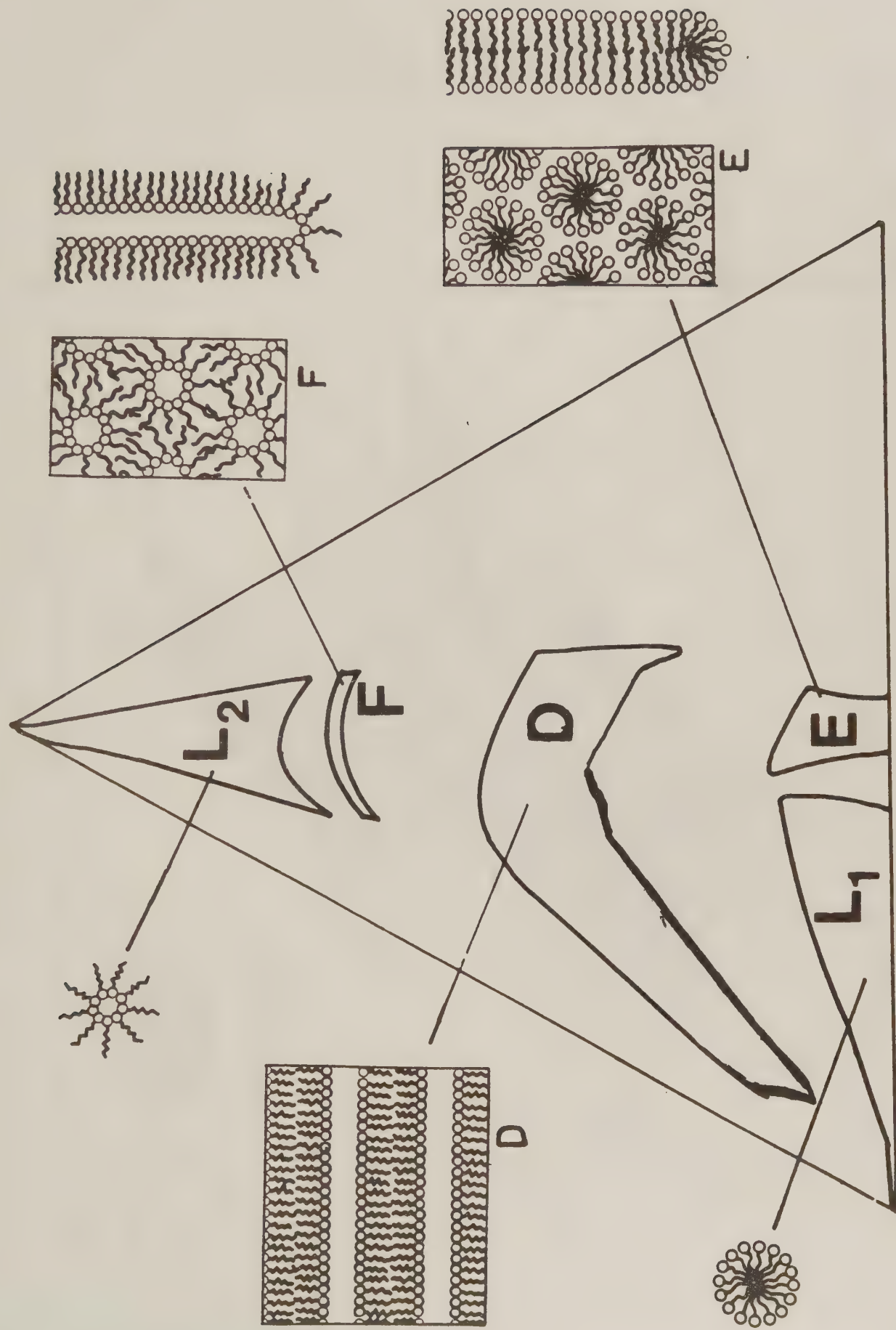
I have had the honour to interact with several skillful scientists in Lund. I can just express a deep and sincere thanks to ALL OF YOU for encouragement, cooperation, criticism and help during this work.

I would also like to thank my wife, Annariikka, for all her support during this work.

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Decanol

FIGURE I



Water

Sodium octanoate

FIGURE 2.

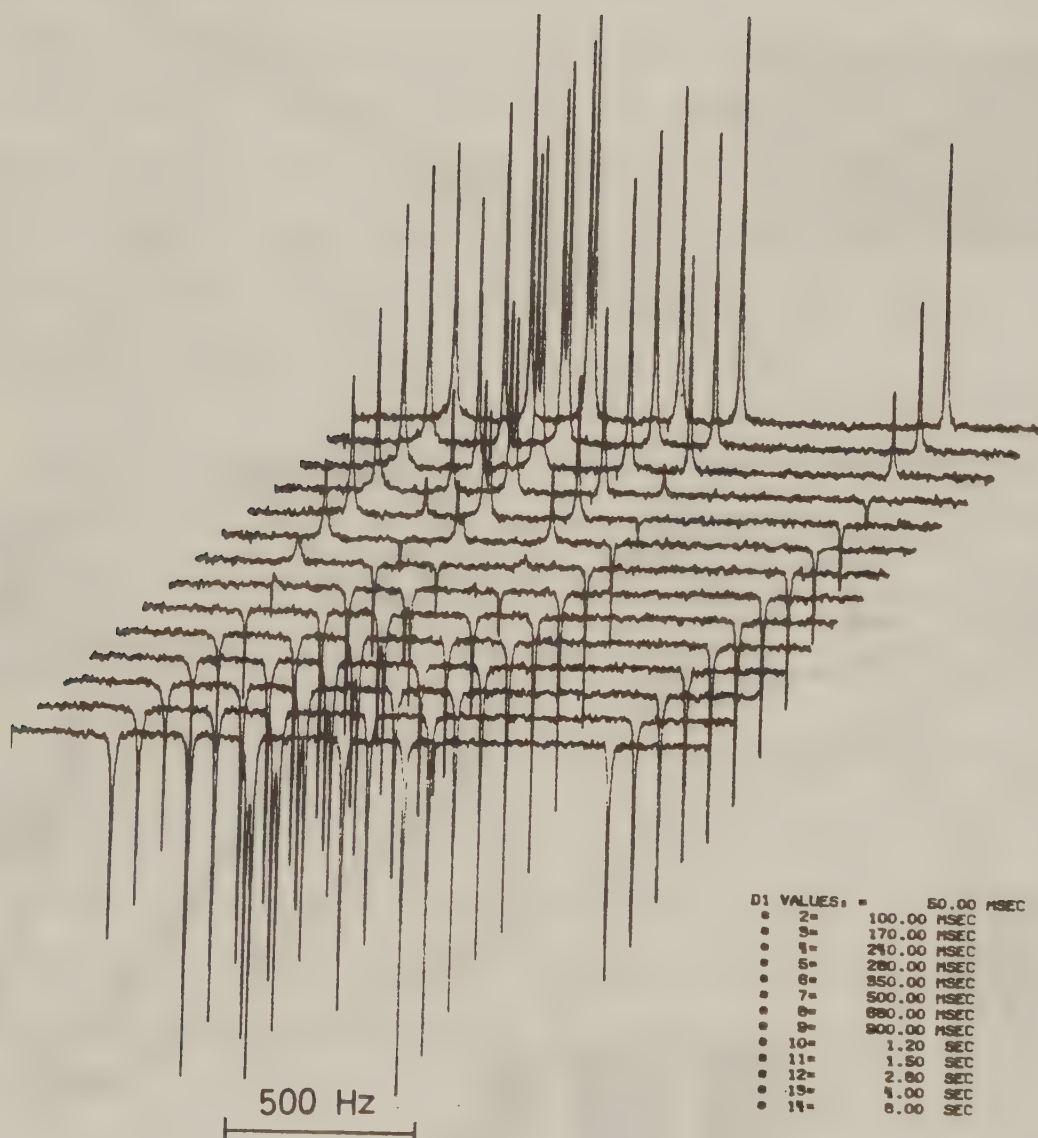
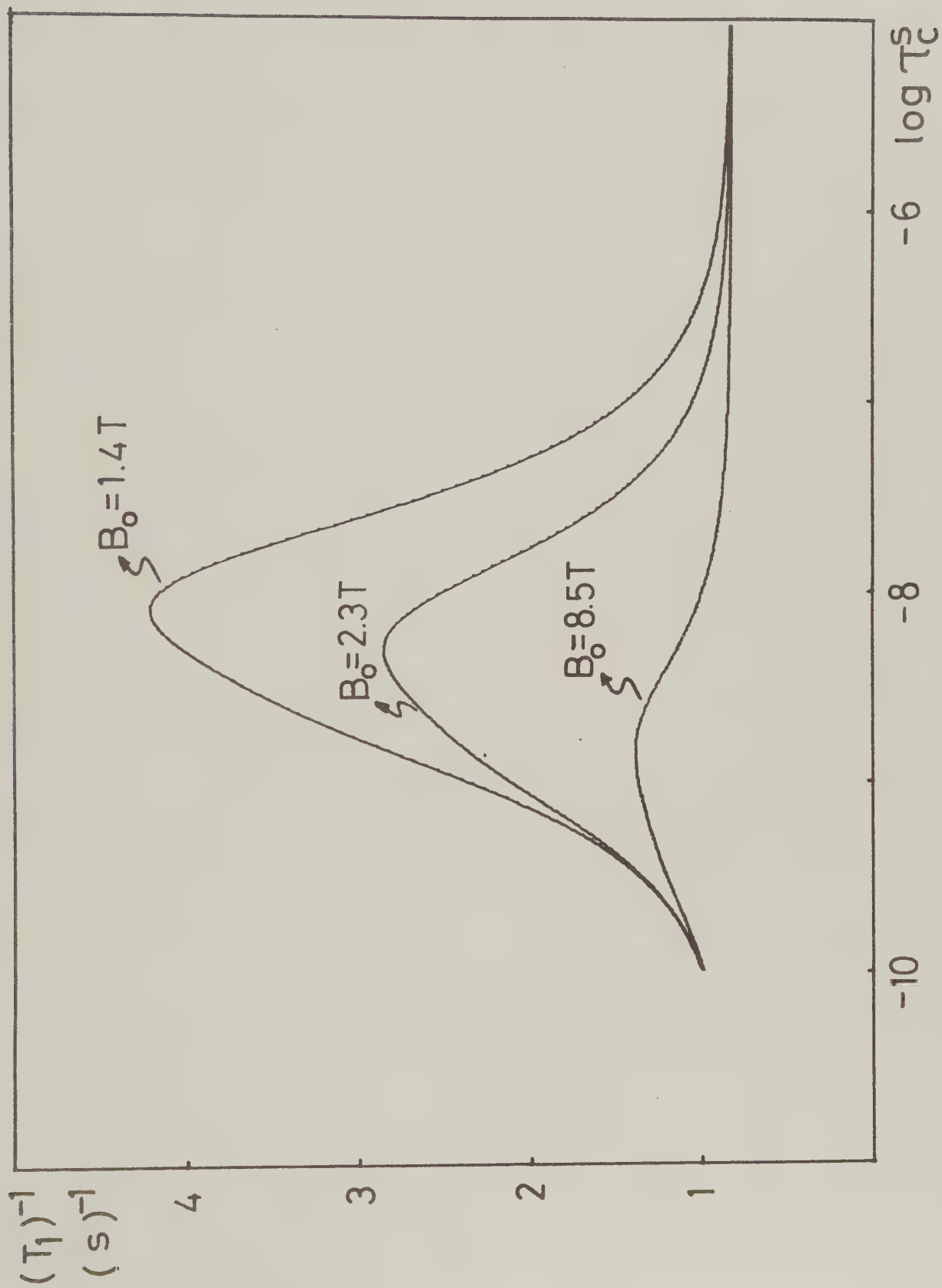


Figure 3.



Carbon-13 Nuclear Magnetic Resonance Relaxation in Microemulsions. Aggregation in the Extensive Solution Phase of the Sodium Octanoate–Octanoic Acid–Water System

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The longitudinal NMR relaxation time for ^{13}C is determined at three different magnetic fields in the extensive solution phase (L_2 region) of the system sodium octanoate–octanoic acid–water. This phase serves as a suitable simple model for microemulsions. The data are analyzed by using a model that emphasizes the separation of the fast internal motions within the aggregates and slow motions on a time scale characteristic of the aggregate dimensions. Three important parameters are derived from the relaxation data: a correlation time characteristic of the fast motion, an order parameter, and, finally, a correlation time for the slow motions. These three parameters show that the internal motion is fast (time scale, 2×10^{-11} s), that the packing is insensitive to water content, and, finally, that the aggregates grow in size up to a certain water content. At higher contents, the simple model with closed water domains does not apply.

Introduction

In three-component systems surfactant–solubilize–water, several different phases with different structures appear.¹ Of these, the normal micellar solutions and the liquid crystalline phases have been studied extensively (for several reviews, see refs 2 and 3). Two very important generalizations emerge from these studies: first, one can rationalize and predict the phase behavior from arguments concerning the geometrical structure of the molecules^{4–6} and, second, local molecular interactions are quite independent of changes in aggregate size and geometry.^{7–9}

In certain amphiphilic solutions, isotropic solutions can simultaneously contain relatively large amounts of hy-

drocarbon and water. For a four-component system with surfactant + cosurfactant having this feature, one often uses the term microemulsion.¹⁰ Many other surfactant

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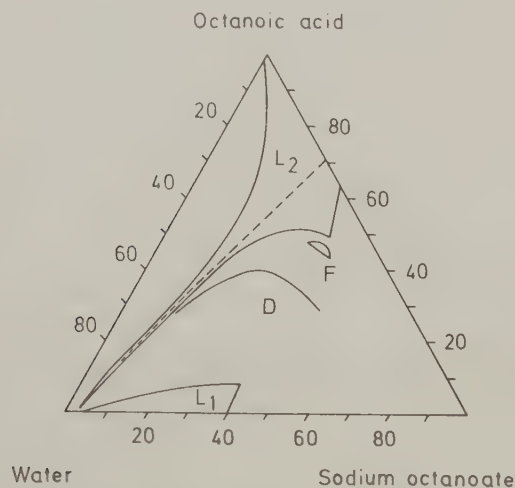


Figure 1. Phase diagram (at 25 °C) of the system sodium octanoate-octanoic acid-water showing the one-phase areas. The full phase diagram is presented in ref 1. The compositions of the samples investigated in this study fall on the dashed line.

systems are closely related to these four-component systems and it was natural to propose a definition of microemulsions that includes all thermodynamically stable single-phase isotropic solutions composed of surfactant, oil, and water.¹¹ As opposed to the normal micelles and lyotropic liquid crystals, the phase structure of microemulsions is generally not very well understood. This is due to the fact that many of the experimental methods used when studying normal micelles do not apply for microemulsions because of the strong aggregate-aggregate interactions in these systems.¹²

In the "atypical" three-component system sodium octanoate-octanoic acid-water, the L_2 solution (using Ekwall's terminology¹) region (Figure 1) is very large, making it a typical microemulsion, although of relatively low complexity, since the system has only three components. Consequently, we have chosen this system as a model system for microemulsions in attempting to determine the structure of these solutions. One experimental technique often employed when studying molecular aspects of amphiphilic systems is ^{13}C NMR, a main advantage being that one is monitoring the unperturbed system. Chemical shift measurements have been used to study normal and reversed micelles.¹³⁻¹⁵ ^{13}C T_1 measurements have been used extensively¹⁶⁻¹⁸ to monitor the dynamics of amphiphilic aggregates. Recently, a theory for the relaxation of ^{13}C in a microdynamically heterogeneous system like an amphiphile system was presented and applied to normal micelles.¹⁹ The present report is an attempt to apply this theory to a complex amphiphilic system where one does not know the structure of the aggregates or, indeed, if there are any aggregates present at all.

One problem with ^{13}C NMR in a multicomponent system is difficulties in distinguishing between the ^{13}C signals from different carbon-containing components. This problem does not arise in the sodium octanoate-octanoic acid-water system since the rapid exchange of protons will ensure that the octanoic acid and the octanoate have common NMR signals. This is one reason for the choice of system, and another is its inherent interest as a model system for microemulsions.

Experimental Section

The measurements were performed at three magnetic field strengths: 15.1 MHz (1.40 T) with a JEOL FX-60, 25.1 MHz (2.34 T) with a Varian XL-100, and 90.5 MHz (8.5 T) with a Nicolet NIC-360. A typical result of a T_1 measurement at the highest field strength is shown in Figure 2.

The protons were decoupled. To avoid heating of the samples due to the decoupling field at the highest field strength, bilevel decoupling was employed. The T_1 values were measured with the fast inversion recovery technique (FIRT).²⁰ The final T_1 values were obtained from a three-parameter fit of the FIRT data to the equation

$$I = I_0(1 - A \exp(-\tau/T_1)) \quad (1)$$

where I_0 and I are intensities of the NMR signal at equilibrium and at a delay time of τ , respectively. A is a constant.

In the conventional 180° - τ - 90° sequence used to determine T_1 , inaccuracies in the pulse lengths and inhomogeneity in the rf field cause phase errors in the transformed spectra, especially at low values of τ . To avoid this problem, we have used the alternate phase method,²¹ i.e., alternating the phase of the 90° pulses, for the two lowest fields. A composite 180° pulse²² together with phase alternation for the 180° pulse was used at the highest field. No phase errors at short τ values could be detected at any of the three fields used. The experimental temperature was 28 °C throughout.

The samples were prepared by weighing the substances into glass tubes. These were then shaken vigorously. Before being measured, the samples were kept at 25 °C for at least 1 week to ensure that they had reached equilibrium.

Theory

We will not derive the appropriate equations used when analyzing the ^{13}C T_1 data since this is done in detail in ref 19. We will, however, state the underlying assumptions. The characteristic property of amphiphilic molecules is that they form aggregates when dispersed in water, two examples being the normal and reversed micelles. The basic assumption when deriving the theory is then a division of the motions giving relaxation into one fast local motion that is anisotropic, and one slow isotropic motion due to aggregate tumbling and/or amphiphile diffusion over the curved surface of the aggregates. There is substantial evidence that the local motions are independent of aggregate structure,^{23,24} and that they do not give rise to local isotropy is evidenced by the occurrence of quadrupole splittings in lyotropic liquid crystals.^{8,25} The fact

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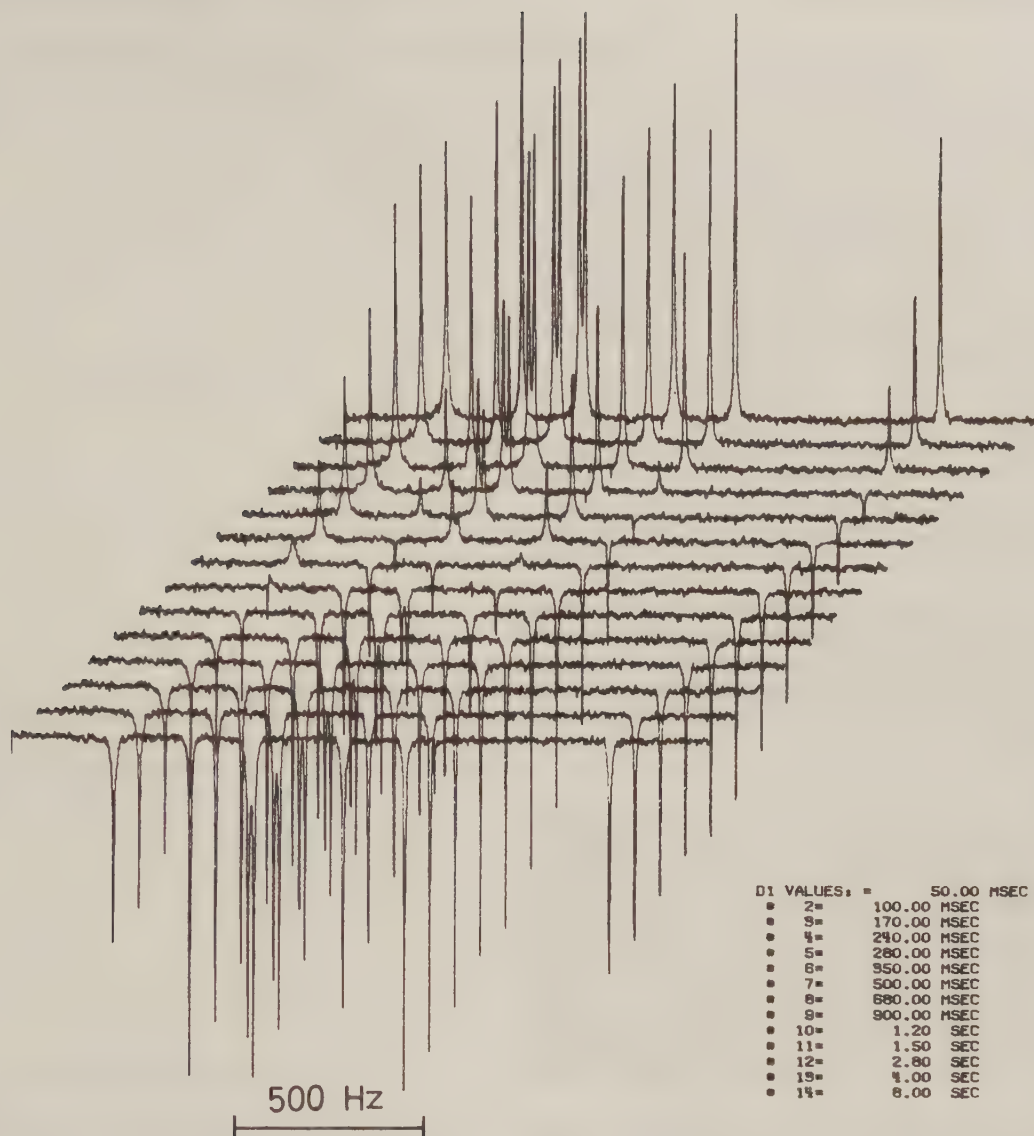


Figure 2. Result of a FIRT experiment performed at 8.5 T. The content of heavy water is 67.5%. From left to right, the peaks in the spectra represent carbons 2, 6, 4, 5, 3, 7, and 8. The carbons are numbered with the polar head group as 1 and the methyl group as 8.

that ^{13}C T_1 's in micellar systems are often shorter than those in the monomeric state is explained by the contribution of slow motions to the relaxation. The basic equation is then (for a CH_2 group subject to proton decoupling)

$$\frac{1}{T_1} = \left[\frac{\mu_0 \hbar \gamma_C \gamma_H}{4\pi r_{\text{C-H}}^3} \right]^2 \left\{ 2(1 - S^2)\tau_c^f + S^2 \frac{1}{5} \left\{ \frac{3\tau_c^s}{1 + \omega_c^2 \tau_c^{s2}} + \frac{\tau_c^s}{1 + (\omega_H - \omega_C)^2 \tau_c^{s2}} + \frac{6\tau_c^s}{1 + (\omega_H + \omega_C)^2 \tau_c^{s2}} \right\} \right\} \quad (2)$$

where S is a local order parameter, describing the anisotropy of the fast local motion. S is defined as the time average

$$S = \frac{1}{2} \langle (3 \cos^2 \theta_{\text{MD}} - 1) \rangle \quad (3)$$

where θ_{MD} is the angle between the local symmetry director and the C-H bond. τ_c^f and τ_c^s are the correlation times for the fast and slow motions. $r_{\text{C-H}}$ is the proton-carbon distance, which throughout this work is given the value 1.09 Å, and μ_0 , $\hbar$, γ_C , and γ_H have their usual meaning. It should be pointed out that we have neglected contri-

butions from amphiphilic molecules that are not associated into aggregates, for example, amphiphiles that are tumbling isotropically in a hydrocarbon environment.

According to the simple theory,¹⁹ ^{13}C relaxation is then determined by the three quantities τ_c^f , S , and τ_c^s , and one needs at least three independent data on relaxation for an interpretation to be possible. In this work, we have preferred to measure T_1 at three different magnetic fields to obtain τ_c^f , S , and τ_c^s . T_1 according to eq 2 is plotted in Figure 3 for typical values of S and τ_c^f . Note that one would expect a frequency dependence over a large range of τ_c^s . Alternative procedures are to combine T_1 data with measurements of T_2 , the transverse relaxation time, or with NOE, the nuclear Overhauser enhancement factor. Single-field ^{13}C relaxation studies of amphiphile aggregates are abundant in the literature (e.g., ref 17, 18, and 26-28) but can apparently not be used directly to extract information on chain flexibility or chain order. It is important to note that deductions made from "effective" correlation times are not justified. In order to write an effective

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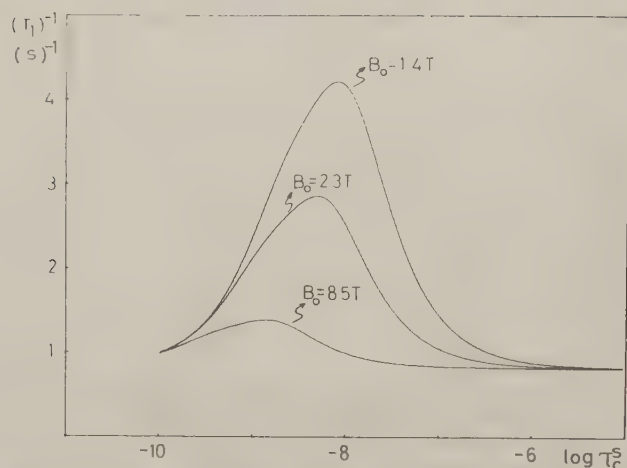


Figure 3. Equation 2 plotted for three different field strengths. The order parameter S is set at 0.2 and the fast correlation time τ_c^f at 2×10^{-11} s.

correlation time as a sum of two or more correlation times, the following two criteria have to be fulfilled for the motions that the correlation times describe. First, the different motions have to be independent and, secondly, they have to modulate the same part of the dipolar interaction.^{29,30}

Results

The ^{13}C T_1 's were measured at three magnetic field strengths for samples in the L_2 region of the sodium octanoate–octanoic acid–water system (Figure 1). The ratio octanoic acid–sodium octanoate was kept constant at about 2.3 (based on weight) and the amount of water was varied (see Figure 1). To exemplify the results, the T_1 's for carbons 2, 4, and 8 are presented in Figure 4. The carbons are numbered with the polar head group as 1 and the methyl group as 8. From these values and eq 2, the three parameters τ_c^f , S , and τ_c^s are obtained at different water contents.

According to the model presented in the Theory section, the value of τ_c^s should be constant for all carbons along the chain at a given concentration. However, from the experimental data using a direct three-parameter fit, we find a variation in τ_c^s of up to 50%. Assuming that the model is correct, this reflects the inaccuracy in the experimental data in combination with strongly varying contributions of the slow motion for different carbons. Thus, one should note that, in eq 2, τ_c^s is multiplied by S^2 , giving little weight to τ_c^s in the fitting of the data for carbons with low S . To minimize the uncertainty in τ_c^s , we have therefore devised the following procedure.

First, as can be seen in Figure 4, the change in T_1 with increasing water content is quite smooth. There are no irregular variations, probably due to the lack of sudden changes in either of the three parameters determining T_1 . With this in mind, we have made a visual fit to the experimental data and assigned the deviation in the experimental data from the fitted line to experimental uncertainties. The data used when evaluating the three parameters are then taken from these fitted lines (see Figure 4). Two methods for evaluating τ_c^f , S , and τ_c^s have been used. In the first, eq 2 is solved for τ_c^f , S , and τ_c^s . These values are shown in Table I for carbon 2. The values of τ_c^f and S are relatively insensitive to τ_c^s ; this is shown in Table II, where we have assigned τ_c^s two different values and calculated τ_c^f and S for carbons 2 and 6, using ex-

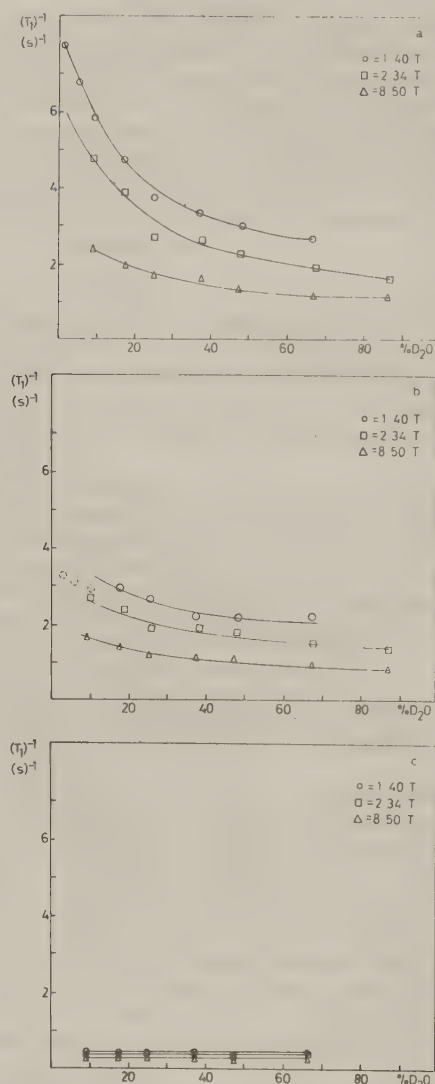


Figure 4. Experimental values of $(T_1)^{-1}$ plotted as a function of the heavy-water content at three different field strengths: (a) carbon 2, (b) carbon 4, and (c) carbon 8. At low water contents, peaks 4 and 5 are not resolved at the lowest field strength. Therefore, the dashed circles in b represent $(T_1)^{-1}$ as measured by the joint peak of carbons 4 and 5.

TABLE I: Values of S , τ_c^s , and τ_c^f Obtained by a Three-Parameter Fit for Carbon C_2^a

D_2O , wt %	S	$10^8 \tau_c^s$, s	$10^{10} \tau_c^f$, s
5	0.33	0.16	0.28
7.5	0.32	0.12	0.27
10	0.31	0.15	0.25
15	0.26	0.17	0.28
20	0.20	0.31	0.35
25	0.18	0.40	0.34
30	0.16	0.55	0.34
40	0.15	0.69	0.30
50	0.15	0.47	0.25
60	0.14	0.65	0.24

^a See under Results for details.

perimental T_1 's taken at 50% water. The values so obtained for τ_c^f and S are then used together with the three different T_1 values obtained for each carbon along the hydrocarbon chain, and a least-squares fit is made to evaluate τ_c^s , assuming that it does not vary along the chain.

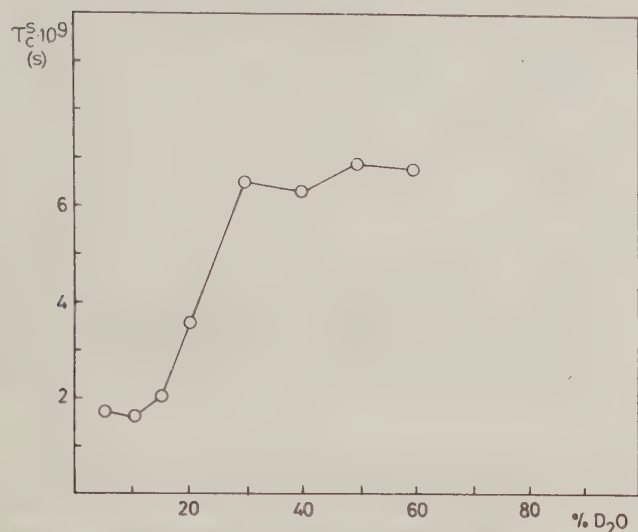
In the second method, we have used the same assumption, i.e., that τ_c^s is constant along the hydrocarbon chain. We then have 15 parameters, τ_c^f , and S for each carbon and one common τ_c^s . To determine these parameters, a

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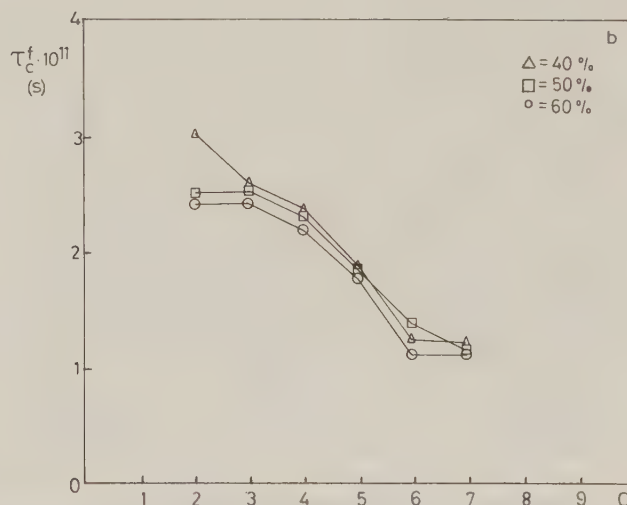
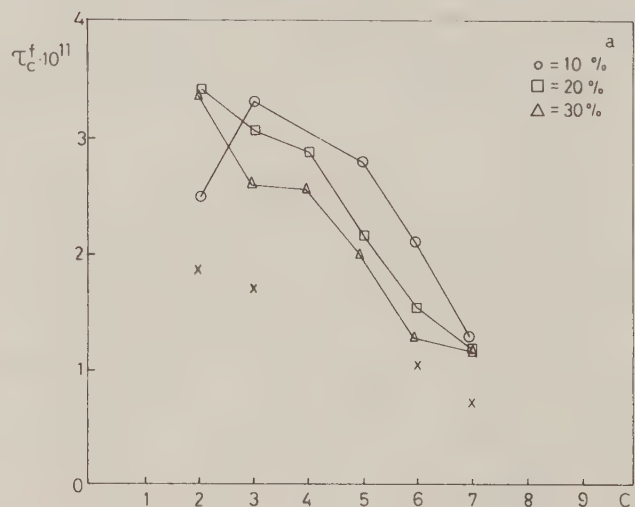
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TABLE II: Influence of τ_c^s on S and τ_c^f for Two Different Values of τ_c^s

	$\tau_c^s = 0.60 \times 10^{-8}$ s		$\tau_c^s = 0.932 \times 10^{-8}$ s	
	S	$10^{10} \tau_c^f$, s	S	$10^{10} \tau_c^f$, s
C_2	0.158 ± 0.007	0.33 ± 0.03	0.154 ± 0.00003	0.356 ± 0.00001
C_6	0.107 ± 0.003	0.152 ± 0.009	0.104 ± 0.008	0.16 ± 0.02

Figure 5. Deduced value of the slow correlation time τ_c^s as a function of the heavy-water content. See text for details.TABLE III: Values of τ_c^s Obtained by a One-Parameter Fit as a Function of Weight Percent D_2O

D_2O , wt %	$10^8 \tau_c^s$, s	D_2O , wt %	$10^8 \tau_c^s$, s
5	0.17 ± 0.01	30	0.65 ± 0.03
10	0.16 ± 0.01	40	0.64 ± 0.05
15	0.21 ± 0.02	50	0.69 ± 0.04
20	0.36 ± 0.03	60	0.68 ± 0.04

Figure 7. Fast correlation time τ_c^f for the different carbons at six different water contents. The data points marked with X refer to monomeric sodium octanoate in heavy water. Data are taken from ref 19.

method. The calculated τ_c^s is given as a function of water content in Table III and plotted in Figure 5. Figures 6 and 7 show the order parameter profile and τ_c^f along the hydrocarbon chain for some water contents.

Discussion

There are two general important observations that can be made from the data in Figure 4. First, there is a field dependence over the entire range of water concentrations. Secondly, this dependence is largest for carbon 2 and decreases along the chain to be smallest for carbon 8. This field dependence demonstrates the contribution to relax-

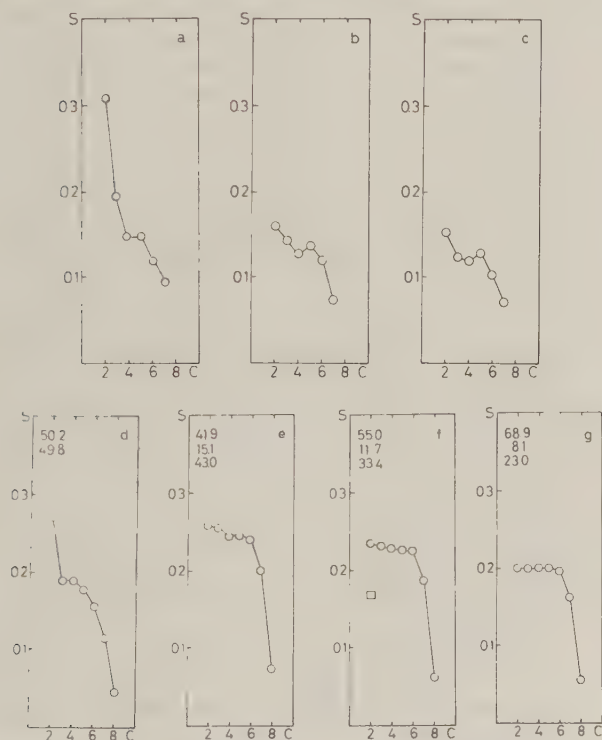


Figure 6. Order parameter profiles for three different heavy-water contents: (a) 10%, (b) 30%, and (c) 50%. Order parameter profiles for three points in the D phase (e-g) and one point in the E phase (d) of the system sodium octanoate-decanol-water. The compositions in weight percent of H_2O , sodium octanoate, and decanol, respectively, from top to bottom, can be seen at the top left-hand corner of the figures. In f, the order parameter ($\square$) of carbon 2 for a point in the D phase of the sodium octanoate-octanoic acid-water system is shown which has the same composition on a molar basis as that given in the figure.

least-squares fit is made by using the entire set of experimental data, i.e., the 21 T_1 's (three for each carbon along the chain). The two methods gave approximately the same results and the data quoted are obtained by using the first

ation from slow motions and strongly suggests the presence of aggregates of some type over the entire concentration region. These aggregates have lifetimes which are not shorter than the correlation time for the slow motion, i.e., a few nanoseconds or longer. We will now discuss the three parameters τ_c^f , S , and τ_c^s separately.

Fast Correlation Time, τ_c^f . The fast correlation time is presented in Figure 7 together with the corresponding values for monomeric sodium octanoate in water taken from ref 19. As can be seen, the fast correlation time is decreasing somewhat along the chain and is relatively insensitive to the amount of water present. τ_c^f of carbon 2 is about 50% larger than the corresponding value for the monomer in water. This difference decreases along the chain and is quite small for carbon 7. These observations presumably reflect the (relatively small) motional restriction of the head group due to its anchoring at the hydrophilic-hydrophobic interface. Our data clearly indicate that the internal motions of the alkyl chains in the aggregates are on the same time scale as for the free monomer.

Already in 1936, Hartley³¹ proposed that the interior of spherical micelles is liquidlike. This is supported by thermodynamic measurements³² that describe the interior of the micelle as a liquid hydrocarbon. Our data provide a direct demonstration that the local molecular motions are only slightly influenced by aggregation and by phase changes between different aggregate geometries.

In conclusion, the interior of the aggregates formed in the L_2 region of sodium octanoate-octanoic acid-water is liquidlike and the intramolecular motions are quite fast, only slightly slower than for monomeric sodium octanoate in water.

Order Parameter, S . The order parameter profiles are presented in Figure 6. For comparison, we also present the order parameter profile for three different points in the lamellar phase and one in the hexagonal phase of the system sodium octanoate-decanol-water.⁸ Although the systems are different, it is instructive to compare trends within the two systems. With reference to Figure 6, the order parameter gradients along the hydrocarbon chain show the following features. The order parameter for carbon 2 is larger than for the rest of the carbons, more so at lower water concentrations. Although the values for carbons 3-5 do not differ much, we do not get the characteristic "plateau" value for high water contents as found in the lamellar phase of the sodium octanoate-decanol-water system, where the order parameter is essentially the same from carbon 2 to carbon 6 (see Figure 6 c,g). The order parameters in the octanoic acid system are smaller than those in the decanol system. As far as we know, no order parameter profiles in the liquid crystalline phases of the octanoic acid system have been determined. However, there are unpublished results for α -deuterated sodium octanoate in the lamellar phase (D) of the sodium octanoate-octanoic acid-water system³³ (included for comparison in Figure 6f). The value obtained is smaller by some 30% compared to the decanol system and corresponds well with the values found at higher water contents in the L_2 phase. The existence of a plateau in the values of the order parameter in the lamellar phase of sodium octanoate-decanol-water, also found in the potassium palmitate-water system,³⁴ corresponds well with the la-

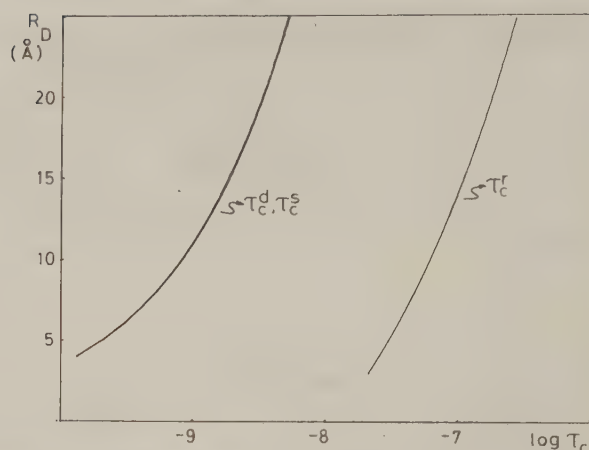


Figure 8. Correlation time for a spherical reversed micelle as a function of the water-core radius. τ_c^f shows the rotational correlation time, τ_c^d shows the correlation time for the diffusion of the amphiphile over the curved surface, and τ_c^s is the sum of these two effects. The parameters used are $\eta = 4.7 \times 10^{-3} \text{ kg m s}^{-1}$, $D = 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and $R_A = 13.5 \text{ Å}$.

mellae having a maximum thickness, or, stated in another way, the area per polar head group is as small as possible; see, for instance, the X-ray data for the decanol system.^{35,36} When the lamellae are thinning, due to either an increase in temperature as in ref 34 or changes in the electrostatic interactions as in ref 8, a larger number of molecular conformations become accessible to the amphiphile and the plateau vanishes. This can also be brought about by changing the geometry to a hexagonal phase since the chains cannot be packed extended in such a geometry.

From this discussion, the following picture of the aggregates in the L_2 region of the sodium octanoate-octanoic acid-water system emerges. At low water contents ($\sim 10\%$), there is a substantial disorder in the hydrocarbon chain but marked motional restrictions near the polar head group supporting the idea³⁷ that rather well-defined complexes are formed. In these, the head groups are linked with hydrogen bonds.^{37,38} As the water content is increased, the profile approaches the plateau-shaped profile. This then indicates that fewer conformations are available for the hydrocarbon chains. The fact that the profile is not fully consistent with a plateau value of the order parameter indicates that the aggregates have an appreciable curvature. Finally, there are no drastic changes in the profile above 20% water pointing toward no drastic changes in the packing of the amphiphilic molecules.

Slow Correlation Time, τ_c^s . In general, when interpreting a correlation time in terms of molecular or, as in this case, aggregate properties, one needs a model for the motion. The model used for interpreting relaxation data in this work ascribes to τ_c^s the overall tumbling of the aggregates and the diffusion of the amphiphilic molecules over the curved surface of the aggregates.

If the aggregates are spherical, one can calculate the correlation time for these motions using the relation

$$\frac{1}{\tau_c^s} = \frac{3kT}{4\pi\eta R_A^3} + \frac{6D}{R_D^2} \quad (4)$$

Here, η is the viscosity of the medium and R_A is the radius

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of the reversed micelle, i.e., the sum of the radius of the water core and the hydrocarbon chain length, R_D is the radius of the water core, and D is the lateral diffusion coefficient of the amphiphilic molecule; k and T have their usual meaning. Using the value 4.7 cP^{39} for η and $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for D ,⁴⁰ we have plotted the correlation times for the two motions in Figure 8. Due to the high value of the viscosity, the contribution from the aggregate reorientation is negligible. The assumption that the aggregates are spherical amounts to saying that the L_2 region is composed of "classical" reversed micelles, i.e., a closed water core immersed in an organic environment. The increase in τ_c^s with increasing water content (see Figure 5) indicates a growth of the water core up to about 40% at which point it levels off with a value of R_D equal to 30 Å. There are a few possible explanations for this behavior, one of which is the ceasing of the aggregate growth. A second, perhaps more plausible, explanation is that there is an onset of a gradual change in solution structure at this water content, introducing contributions from other slow isotropic motions. However, there is no way in which we a priori can say anything about the shape of the aggregates formed. It has been suggested³⁸ that, in the region between 20–40%, there is a solution of reversed micelles and that, at 40%, there is a transition to aggregates of the normal type. In part, these observations are in line with a recent multicomponent self-diffusion study⁴¹ of the same system. Thus, it was observed that Cl^- co-ions diffuse more slowly than Na^+ counterions at water contents below 40% while at higher water contents the reverse situation holds. However, while the ^{13}C relaxation results emphasize the presence of surfactant aggregates, the self-diffusion study does not show the pattern typical of reversed micelles. Nevertheless, it should be recalled that NMR relaxation and self-diffusion weigh free and associated molecules quite differently. The ^{13}C relaxation results demonstrate that part of the surfactant molecules occur in large aggregates with a lifetime of at least a few nanoseconds but cannot quantify the fraction associated. The self-diffusion results emphasize the relatively facile motion of part of the water molecules and sodium ions over distances larger than any aggregate sizes but cannot exclude the fact that the main part occurs in the aggregates. Taken together, the two studies indicate the presence of reversed micelles below 40% water by weight. The water molecules and ions are not confined to the water cores of these reversed micelles

but occur to a significant extent in the intermicellar solution.

The τ_c^s values by themselves give the following picture: At low water contents, $\sim 10\%$, rather well-defined complexes exist; in an intermediate region, 10–40%, there are aggregates that grow continuously with added water; and finally, there is a leveling off of τ_c^s due to the fact that either the aggregates stop growing or a change occurs in the aggregate geometry.

Conclusion

We feel that the main value of the present study lies in the devised procedure for analysis of ^{13}C relaxation times. It is demonstrated that, from measurements at three different magnetic fields, it is indeed possible to perform an essentially complete analysis using the relaxation equations derived on the basis of the two-step model. This analysis gives three quantities of interest for the characterization and understanding of simple and complex surfactant systems, i.e., one correlation time characterizing the local motions within an aggregate, one correlation time associated with the aggregate dimensions, and, finally, the order parameters (or the order parameter profile) characterizing the state of the alkyl chains. The method is generally applicable to isotropic surfactant systems and of special interest are studies of four-component surfactant + cosurfactant microemulsions and cubic liquid crystals. Such studies are underway.

For the particular case of the L_2 region of the sodium octanoate–octanoic acid–water system, the study of ^{13}C relaxation at three magnetic fields strongly indicates the presence of aggregates; it gives relevant information on the state of the hydrocarbon chains in the aggregates; and finally, it gives us the correlation time for the slow, isotropic motion. The motions within the aggregates are fast and the packing is rather insensitive to the water content. The aggregates grow continuously with added water up to a certain value. After that point, the data cannot tell us whether the aggregates stop growing or whether an onset of change in the aggregate geometry occurs. With reference to other observations, the latter is probably the case.

Acknowledgment. Enlightening discussions with Bertil Halle and Bengt Jönsson are gratefully acknowledged. O.S. thanks "Stiftelsen Bengt Lundqvists Minne" and T.A. thanks Nordiska Ministerrådet for grants. The work was supported by the Swedish Natural Sciences Research Council and the Swedish Board for Technical Development.

Registry No. Sodium octanoate, 1984-06-1; octanoic acid, 124-07-2.

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11

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SURFACTANT ALKYL CHAIN MOBILITY AND ORDER IN MICELLES AND MICRO- EMULSIONS

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The NMR spin-lattice relaxation times (T_1) of ^{13}C were measured in two model surfactant systems, i.e., isotropic solutions of sodium octanoate in water (L_1) and of sodium octanoate and water in octanoic acid (L_2). From the experimental data at three magnetic fields (1.4, 2.3 and 8.5 T), information was deduced on the hydrocarbon chain mobility, order and on slow overall motions. This was achieved by applying the relaxation model of H. Wennerström *et al.*¹. The measurements show clearly a frequency dependent relaxation over the entire concentration range in both systems. The fast local motion in the L_1 phase is comparable to that of the free monomer in water. In the L_2 phase, slightly slower local motions are obtained. As a general trend, the fast local motion is slowest at the headgroup and increases along the chain. The order parameter decreases along the chain towards the nonpolar end. The order parameter profile is quite invariable in the micellar solution but is found to change when water is added to the L_2 solution phase. The slow correlation time is fairly constant in L_1 but changes upon water addition in L_2 . On the whole, the results emphasize the liquid character of the surfactant aggregates, i.e., characterized by low order and rapid molecular motions.

INTRODUCTION

Surfactant liquid crystalline phases are characterized by fast local motions and by long-range order. These characteristics are manifested in static effects in the NMR spectrum and in birefringence. The static effects show that the fast local motions do not average the interactions to zero, i.e. the fast local motions are anisotropic. The static effects contain useful information concerning both the packing of the amphiphile chains and the phase structure. In particular, the order parameter profiles, derived from the ^2H quadrupolar splittings in perdeuterated amphiphiles, have been used extensively to obtain information about chain packing and to test different models for amphiphilic aggregation². In micellar solutions, these static effects are completely averaged out, giving rise to high resolution NMR spectra.

One nucleus often used to probe the properties of micellar solutions is ^{13}C . This is due to the large shift range which makes it possible to monitor almost every carbon along the hydrocarbon chain separately. However, the complex motional behaviour in amphiphile aggregates makes the interpretation of ^{13}C relaxation data difficult. Several theoretical approaches have been devised^{3,4}, but these models tend to be complicated in their application and, in particular, a comparison with results from lyotropic liquid crystals is not easy.

Wennerström *et al.*¹ have developed a relaxation model based on experimental information concerning the motions in micelles. This model can be used to extract from experimental data information about the dynamics and the packing of the amphiphile hydrocarbon chains in the aggregates. Furthermore, a comparison between order parameters of different phases provides structural information of particular interest for isotropic phases of unknown structure, like microemulsions.

In this work, we have applied this "two-step" relaxation model to two systems: ordinary micelles in the sodium octanoate-water system and the extensive solution phase (L_2) in the sodium octanoate-water-octanoic acid system.

EXPERIMENTAL SECTION

Samples were prepared by weighing the substances into NMR tubes. After shaking, the samples were kept at 25°C for at least one week for equilibration. The chemicals used were sodium n-octanoate (99%) and octanoic acid (99%), both from BDH Chemicals Ltd.

The measurements were made at three magnetic field strengths: 1.40 T (15.1 MHz) with a Jeol FX-60 spectrometer, 2.34 T (25.2 MHz) with a Varian XL-100 spectrometer and 8.5 T (90.5 MHz) with a Nicolet spectrometer.

The relaxation times were measured using the Fast Inversion Recovery Technique (FIRT)⁵. The T_1 values were obtained by nonlinear least squares fit to Equation (1),

$$I = I_0(1 - Ae^{-\tau/T_1}) \quad (1)$$

where I_0 and I are the intensities of the NMR signal at equilibrium and at a delay time τ . A is a constant depending on the pulse repetition time and the pulse angle. For further details concerning the experimental technique, see Reference (6).

THEORY

Relaxation of carbons in alkyl chains can (in the absence of paramagnetic species) be referred entirely to the modulation of the ^1H - ^{13}C dipolar coupling. The standard equation for analyzing ^{13}C relaxation is

$$\frac{1}{T_1} = \left[\frac{\mu_0 \hbar \gamma_C \gamma_H}{4\pi r_{\text{C-H}}^3} \right]^2 \cdot N \cdot \tau_c \quad (2)$$

Here, τ_c is the correlation time for the motion causing relaxation, N is the number of directly bonded protons and $r_{\text{C-H}}$ is the carbon-proton distance (in this work, given the value of 1.09 Å). μ_0 , $\hbar$, γ_C and γ_H have their usual meaning. Equation (2) assumes a single correlation time in the extreme narrowing range. If two or more fast processes modulate the same interaction or if the modulation of the interaction is nonexponential, it may be permissible to introduce an "effective" correlation time in the data analysis. However, it is immediately found that the application of equations like Equation (2) leads to inconsistencies. Applying Equation (2) to typical experimental micellar T_1 's gives correlation times well in the extreme narrowing range. Experimentally one finds T_1 's that depend on the field strength used¹. In addition, one finds that the Nuclear Overhauser Enhancement (NOE) is lower than its maximal value^{4,7}. It is evident, therefore, that a somewhat more complex relaxation model is needed.

We now proceed to examine the motions that an amphiphilic molecule is expected to undergo in a micelle. It is beyond any doubt that the hydrocarbon core of both liquid crystalline phases and micelles has a liquid-like character^{8,9}. Furthermore, the local

molecular motions appear to be the same in micelles and liquid crystals^{10,11}. In the liquid crystalline phases, these motions are clearly anisotropic as evidenced by the quadrupolar and dipolar splittings. Therefore, the motions of the amphiphile in a micelle are also expected to be locally anisotropic. The frequency dependent T_1 relaxation times imply slow motions which average out the residual interactions. Prime candidates for these motions are micelle reorientation and/or diffusion of amphiphiles over the curved micellar surface.

A simple relaxation model should include fast local motions that are anisotropic and slower motions that are isotropic and due to aggregate tumbling and/or lateral diffusion. This is the physical basis of the model derived by Wennerström *et al.*¹

For the detailed derivation of the relaxation expression, the reader is referred to Reference (1). The final expression is

$$\frac{1}{T_1} = \left[\frac{\mu_0 \hbar \gamma_C \gamma_H}{4\pi r_{C-H}^3} \right]^2 \left\{ 2(1-S^2)\tau_c^f + S^2 \frac{1}{5} \left[\frac{3\tau_c^s}{1 + \omega_C^2 \tau_c^s} + \frac{\tau_c^s}{1 + (\omega_H - \omega_C)^2 \tau_c^s} + \frac{6\tau_c^s}{1 + (\omega_H + \omega_C)^2 \tau_c^s} \right] \right\} \quad (3)$$

where τ_c^f and τ_c^s are the correlation times for the fast and the slow motions, respectively, ω_C and ω_H are the resonance frequencies in units of radians per second, and S is the local order parameter defined as the time average

$$S = \frac{1}{2} \langle (3 \cos^2 \theta_{MD} - 1) \rangle \quad (4)$$

Here, θ_{MD} is the angle between the local symmetry director and the C-H bond.

Equation (3) is plotted for the three different magnetic field strengths in Figure(1). Similar expressions can be derived for the NOE factor and T_2 from the theory in Reference (1).

For each carbon, there are three independent parameters, τ_c^f , τ_c^s and S , and hence three independent measurements are needed to solve Equation (3). Since T_2 is difficult to measure for ^{13}C , one is left with NOE and T_1 . In this work, we have chosen to measure T_1 at three different fields.

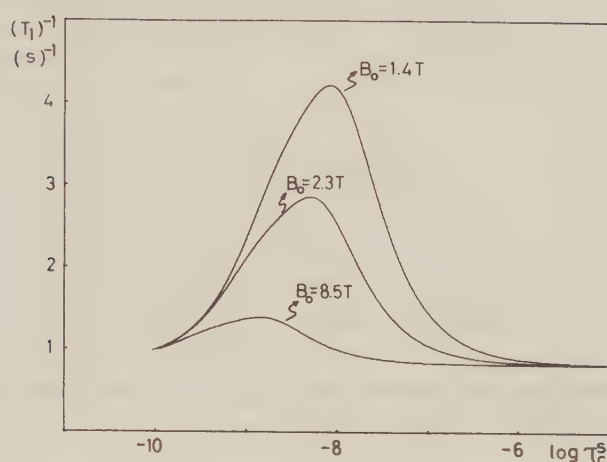


Figure 1. Equation (3) plotted for three different field strengths. The order parameter, S , is set at 0.2 and the fast correlation time, τ_c^f , at $2 \cdot 10^{-11}$ s.

RESULTS AND DISCUSSION

The Micellar Solution Phase (L_1)

The relaxation times are found to be field dependent for samples above the critical micelle concentration (CMC). This manifests relaxation contributions from a slow motion and points to the presence of aggregates in the solution.

The field dependence is largest for the α -carbon i.e., the carbon next to the carboxylate group, and it decreases along the hydrocarbon chain. The relaxation rates $(T_1)^{-1}$ for the α -carbon as a function of the amphiphile concentration and magnetic field strength are shown in Figure (2).

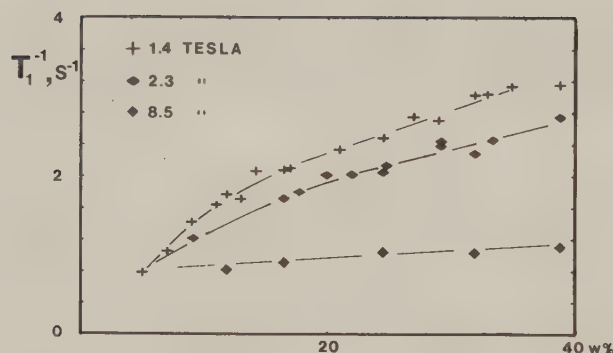


Figure 2. Experimental values for $(T_1)^{-1}$ of the α -carbon as a function of amphiphile concentration.

Relaxation rates above the CMC contain contributions from the micellized amphiphile as well as from the free monomers. In order to separate out the relaxation rates for the micellar monomers, the contribution from the free monomers has to be subtracted. An often used approximation is to assume a constant free monomer concentration (m_f) above the CMC - the pseudo-phase model. However, it is now well documented that m_f decreases above the CMC¹²⁻¹⁴. In a recent theoretical work, Gunnarson et al.¹⁵ have calculated the free monomer concentration above the CMC. If the cell model is used, a marked decrease in m_f above the CMC is found. The complicated thermodynamic equation giving the free monomer concentration can be replaced by a simple equation¹⁶, that closely mimics the correct equation.

$$x = \frac{m_f}{m_t} = \left(\frac{m_{cmc}}{m_t} \right)^{3/2} \frac{v_w}{v_{tot}} \quad (5)$$

where m_f is the molal concentration of free monomer and m_t is the total concentration of amphiphile in the solution. V_w is the volume of the water molecules and V_{tot} is the total volume of both the water and amphiphile molecules.

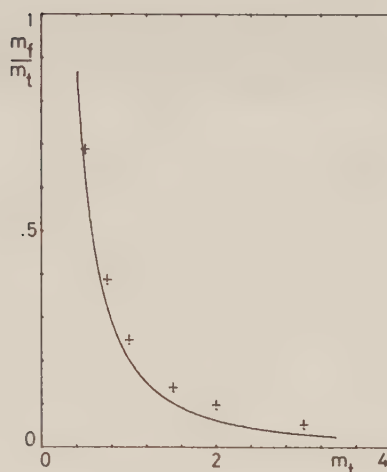


Figure 3. Free amphiphile concentration divided by the total amphiphile concentration. The points are experimental values from self-diffusion studies¹³ on the system sodium octanoate - water. The solid line shows Equation (5) plotted as a function of the amphiphile concentration.

In Figure (3), results from self-diffusion measurements for the system sodium octanoate-water are compared with the theoretical values from Equation (5).

Relaxation rates for carbons in micelles are obtained from

$$R_{\text{mic}} = (R_{\text{obs}} - x R_{\text{mon}}) / (1 - x) \quad (6)$$

where $R = (T_1)^{-1}$. Equation (6) assumes the well-demonstrated fast exchange situation.

Equation (3) is solved by iteration. Within the model, Equation (3) could be solved (i) for each carbon along the chain separately or (ii) by assuming that the slow correlation time is constant along the chain (which it should be); then, the total number of parameters is reduced.

In Figure (4), the fast correlation time (τ_c^f) is shown as a function of chain position and for various amphiphile concentrations. τ_c^f does not vary appreciably with concentration. The uncertainty is ± 4 ps.

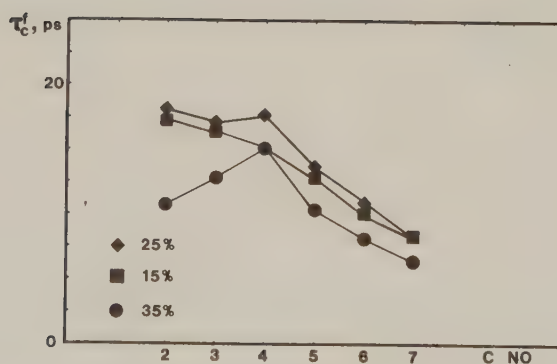


Figure 4. The deduced values for the fast correlation time (τ_c^f) as a function of position in the hydrocarbon chain.

The fast motion is slower at the polar head, indicating anchoring to the surface. Head group - head group and head group - water interactions are mainly responsible for this reduction of the fast motion. As the amphiphile concentration is increased, the electrostatic repulsion between the head groups will decrease which might influence the fast correlation time. The hydration of the micelle is expected to be roughly constant¹⁷. The deduced very rapid motions are in agreement with the classical picture, the liquid-core Hartley micelle¹⁸.

In Figure (5), the order parameter profiles are shown for different amphiphile concentrations. The order parameter profiles are s-shaped, with the largest values for S at the polar head. Both the numerical values of S and the profiles are in agreement with the predictions of Gruen's theoretical model¹⁹. In this model, neither water nor head groups can exist in the micellar core. The

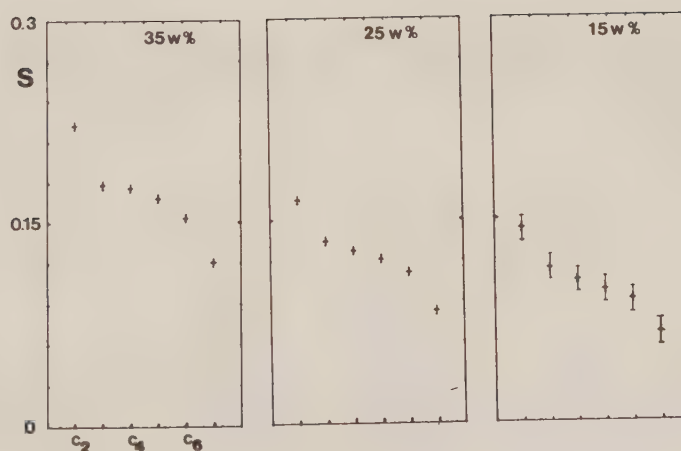


Figure 5. Order parameter profiles at three different amphiphile concentrations.

hydrocarbon chains are assumed to be packed with the same density as in a liquid hydrocarbon. Our findings are also in agreement with experimental results of paramagnetically enhanced ^{13}C -relaxation in this system^{20,21} and other observations²². The order parameter value of the ω -methyl is very low (<0.15) and thus seems not to be consistent with the Dill and Flory model.²³ Aniansson²⁴ has pointed out that protrusion would cause an increase in disorder for the ω -methyl.

An important observation is that the order parameter profile as well as the numerical values at the highest concentrations are very closely the same as those obtained from deuterium splittings in the hexagonal (E) phase²⁵. Results are presented in Table I. In order to compare the order parameters in the E-phase with those in the L_1 -phase, $S(L_1)$ has to be divided by a factor of 2. This follows since the local director in the L_1 -phase makes an angle of 90° with the director of a hexagonal phase.

The molecular order is essentially equal in these two phases, provided that the amphiphile concentration is high in the L_1 phase. An hypothesis that might further be tested is that phases in equilibrium with each other over narrow two-phase regions have the same order parameter values.

Table I. Order parameter values of sodium octanoate in water. A comparison between values obtained from deuterium splittings in the hexagonal phase and values obtained from ^{13}C relaxation in the micellar phase.

Carbon atom number	E-phase	35 wt % L_1 -phase
2	0.130	0.110
3	0.0918	0.089
4	0.0918	0.088
5	0.0861	0.084
6	0.0762	0.077
7	0.0570	0.060
8	0.0221	< 0.05

The slow correlation time (τ_c^s) is shown in Figure (6), as a function of the amphiphile concentration. The slow correlation time is essentially constant since the uncertainty is about $\pm 30\%$.

If one assumes that only rotational and/or lateral diffusion are effective in averaging the residual interaction, theoretical values can easily be compared with the experimental ones. In Figure (7), values calculated from the Stokes-Einstein rotational

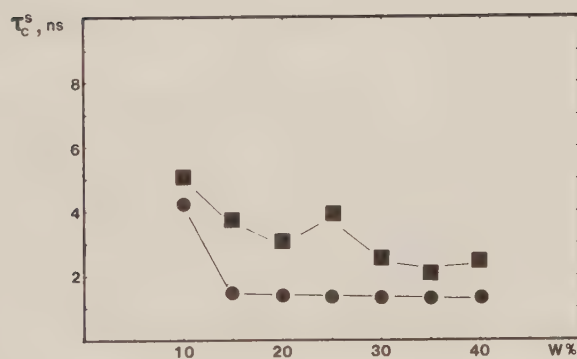


Figure 6. The deduced values for τ_c^s as a function of amphiphilic concentration. ■ indicates that T_1 's for all methylene carbons have been used in the calculation. ● indicates that the T_1 's for the α -carbon (No. 2) only have been used when evaluating τ_c^s .

diffusion equation and the lateral diffusion equation are plotted against aggregate radius.

The Stokes-Einstein equation,

$$\tau_c^R = \frac{4\pi\eta R^3}{3kT} \quad (7)$$

where R is the aggregate radius and η is the viscosity of the medium, assumes hard spheres in a continuous medium. The lateral diffusion equation is given by

$$\tau_c^L = \frac{R^2}{6D_L} \quad (8)$$

where D_L is the lateral diffusion coefficient. For the present system, a value of $2 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ was used²⁶.

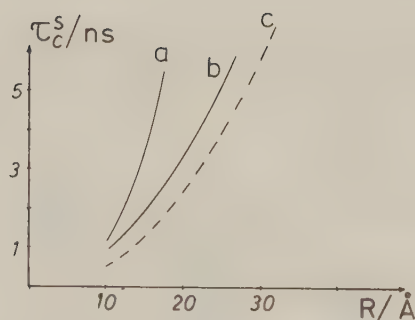


Figure 7. Correlation times (τ_c^s) calculated from rotational and/or lateral diffusion as a function of aggregate radius. (a) denotes only rotational diffusion, (b) denotes only lateral diffusion, and (c) denotes a sum of both lateral and rotational diffusion:

$$\frac{1}{\tau_c^s} = \frac{1}{\tau_c^R} + \frac{1}{\tau_c^L}$$

Aggregate radii of 10-15 Å are obtained from the experimental values if only rotational diffusion is assumed. However, for correlation times in the vicinity of 1 ns, lateral and rotational diffusion give about the same results. Therefore, it is difficult to separate these motions from each other. Experimental results from neutron scattering²⁷, classical light scattering and quasi elastic light scattering²⁸ show that the aggregation number and the radius increase when the amphiphile concentration is increased. We could not detect this in the slow correlation time, perhaps due to the high uncertainty, but both the fast correlation time and the order parameter are concentration dependent.

Besides lateral and rotational diffusion, other mechanisms might influence the slow correlation time. For short chain amphiphiles, monomer exchange^{14,29} and protrusion²⁴ could affect τ_c^s , especially near the CMC.

Large deviations from the assumed spherical aggregate to rod-like form would change the relaxation behaviour completely and can be excluded. Since S and τ_c^f are shown⁶ to be quite insensitive to moderate changes in τ_c^s , we believe that our approximation is reasonable.

The Water-Poor Solution Phase (L_2)

T_1 relaxation times were measured at three different magnetic field strengths for the L_2 solution phase of the microemulsion model system, sodium octanoate - octanoic acid - heavy water. The molar ratio between octanoic acid and sodium octanoate was kept constant at 2.65 and the amount of water was varied. The phase diagram, determined by Ekwall *et al.*³⁰ is shown in Figure (8).

Experimental relaxation rates of the α -carbon are shown in Figure (9). A clear frequency and composition dependence is seen. This suggests that there are aggregates in the solution and that their nature changes with the water content. The relaxation rates were used in further calculations without corrections for contributions from free monomers, which can be assumed to be small. Solving Equation (3) by iteration, we obtained values for the fast and slow correlation times and the order parameter. The fast correlation times are shown as a function of water content in Figure 10.

The motion is, as in the micellar L_1 solution phase, slowest at the polar head, demonstrating the anchoring of the polar head. The fast motion is slower than for monomeric sodium octanoate in water and slower than for micellar octanoate in the L_1 solution phase. The fast correlation time profile is steeper than in the L_1 solution phase. This could be interpreted as weaker chain-

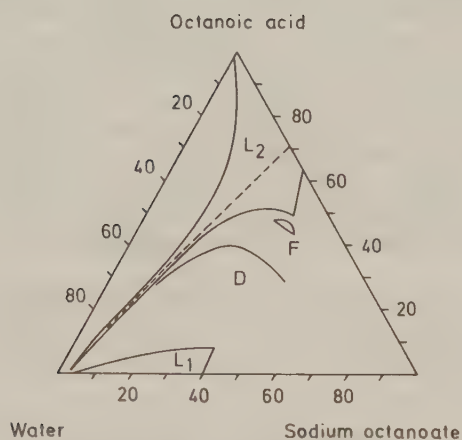


Figure 8. The three-component phase diagram sodium octanoate-octanoic acid-water (redrawn from Reference 30). The composition of the samples studied follows the dotted line.

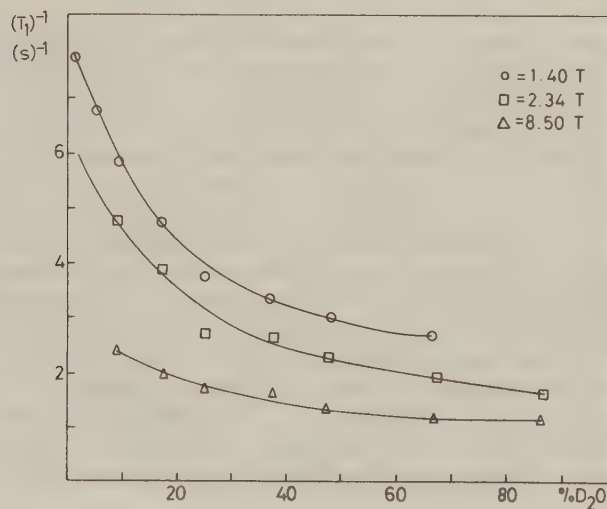


Figure 9. Relaxation rates for the α -carbon as a function of heavy water content (weight percent) at three different magnetic fields. The molar ratio between octanoic acid and sodium octanoate was kept constant at 2.65.



Figure 10. The fast correlation time at four different water contents. X indicates the correlation time for monomeric sodium octanoate in water.

chain interactions. The high values of τ_c^f close to the polar head observed at low water contents, indicate a marked motional restriction for the head-group.

At low water contents, a nearly exponential decay of the order parameter is observed, see Figure 11. The absence of a plateau, observed in the lamellar phases³¹ would, along with the reasoning of Marcelja³² and Levine³, suggest that steric repulsions between chains are relatively insignificant. Thus the chains should behave roughly as isolated chains. No odd-even alternation in the order parameter^{33,34} is observed, so the molecular axis should be the axis of symmetry. At higher water contents, a reduction of the order and a more plateau-like profile are obtained.

We now proceed to compare and discuss order parameter values and profiles in different phases. At high water contents, the L_2 phase is in equilibrium with the lamellar D phase. The order

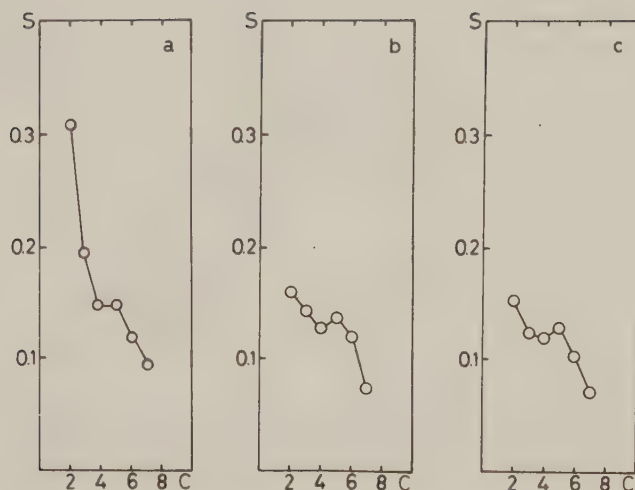


Figure 11. The order parameter profiles at three different water contents: (a) 10 wt%, (b) 30 wt% and (c) 50 wt% in the L_2 solution phase.

parameter values in this part of the L_2 phase are much lower than those found in the lamellar D phase of the system sodium octanoate - decanol - water³¹. On the other hand, unpublished results for α -deuterated sodium octanoate in the lamellar phase of the system sodium octanoate - octanoic acid - water³⁵ agree very well with the values found in the L_2 phase. This is shown in Figure (12). Decanol seems to have a different effect on the octanoic chain order than octanoic acid. The alcohol enhances, while the acid reduces or maintains, the chain order. This has important implications for understanding phase stability. As argued above, if the tie-lines are short between two phases, one expects to find similar order parameter values and profiles of adjacent samples.

The slow correlation time, τ_c^s , is shown as a function of water content in Figure 13. As the water content is increased, the motion is slowed down. The slow motion is assumed to consist of an overall tumbling of the aggregate and/or the diffusion of the

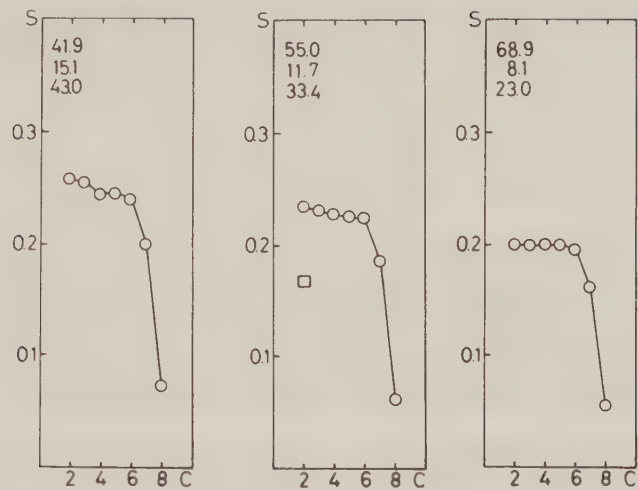


Figure 12. Order parameter profiles³¹ of octanoate at three different concentrations in the lamellar (D) phase of the system sodium octanoate-decanol-water. $\square$ indicates the corresponding value of the α -carbon³⁵ in the system sodium octanoate-octanoic acid-water. The composition is given in wt% in the order water, sodium octanoate and decanol or octanoic acid.

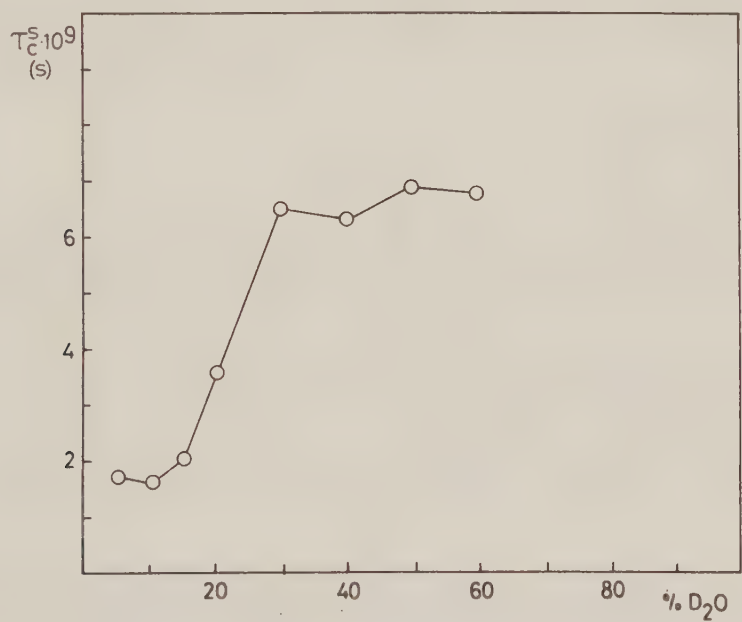


Figure 13. The slow correlation time as a function of the heavy water concentration.

amphiphile over the curved surface of the aggregates. If the aggregates are spherical and noninteracting and the motions are uncorrelated, one has

$$\frac{1}{\tau_c^s} = \frac{3kT}{4\pi\eta R_A^3} + \frac{6D_L}{R_D^2} \quad (9)$$

where η is the viscosity of the medium taken as 4.7 cP ³⁶. R_A is the radius of the aggregate, R_D is the radius of the water core and D is the lateral diffusion coefficient of the amphiphile molecule taken to be $2 \cdot 10^{-10} \text{ m}^2\text{s}^{-1}$ ²⁶. The amphiphile molecular length is taken to be $13.5 \text{ \AA}$. The theoretical value of the slow correlation time as a function of R_D is plotted in Figure (14).

Comparing the theoretical values with the experimental ones, one finds that the contribution from aggregate reorientation is

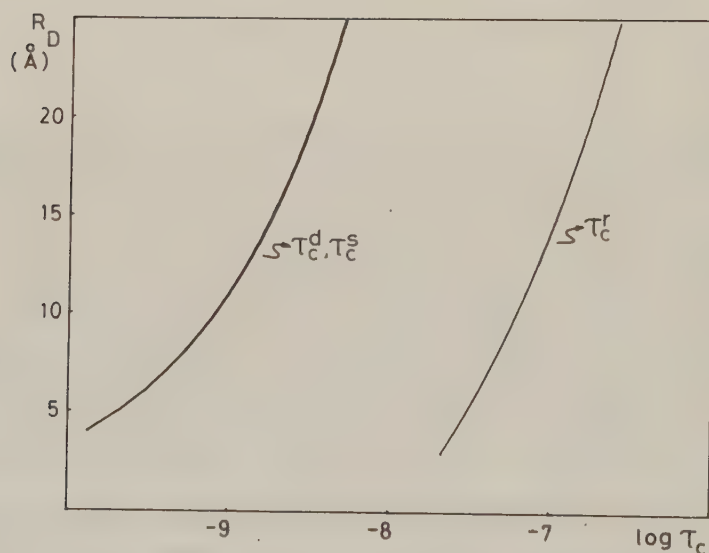


Figure 14. The theoretical value of the radius R_D as a function of the slow correlation time.

negligible. The τ_c^s values indicate a growth of the water core for concentrations up to 40% water where the radius should be about 30Å. At high water contents, no change in τ_c^s is seen. At very low water contents, τ_c^s corresponds to an aggregate radius of an extended octanoate chain. This gives further evidence for the existence of small complexes at the low water concentrations^{37,38}. Hydrogen bonds are argued to stabilize these complexes. This is also supported by the high order parameter values of the α -carbon found at these concentrations.

It has been suggested³⁸ that reversed micelles exist in the concentration range 20-40% water and that a transition to normal micelles occurs above this concentration. Our results support a decrease of the aggregate curvature up to 40% water. Above this concentration, nothing dramatic happens when water is added.

Self-diffusion studies³⁹ show a continuous increase in the diffusion of all components upon the addition of water. This agrees well with the decrease of the order parameter. The Cl^- coions were found to diffuse slower than the Na^+ counterions at water concentrations below 40wt %, a further indication that reversed micelles are present at these concentrations.

The following picture emerges: At low water contents (<10 wt %) rather well-defined complexes exist; in an intermediate region (10-40 wt %), there are aggregates that grow continuously with added water; and finally, there is a levelling off of τ_c^s due either to the fact that the aggregates stop growing or that a change occurs in the aggregate geometry.

CONCLUSIONS

The present study shows that new insight into the structure and dynamics of micellar solutions and microemulsions can be obtained from multi-field ^{13}C NMR relaxation studies.

The analysis of the ^{13}C relaxation times was performed by means of a two-step motional model, which seems to be adequate. This is supported by the close agreement in order parameter values between the L_1 micellar phase and the E hexagonal liquid crystalline phase. Moreover, theoretical predictions of the Gruen model¹⁹ are in agreement with our results in the micellar phase.

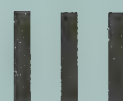
For the water-poor solution phase (L_2) of the system sodium octanoate-octanoic acid-water, order parameter profiles are different from other phases that are not in equilibrium with the L_2 phase. It is demonstrated that a comparison of order parameter

values and profiles of different phases gives insights into structural features of microemulsions.

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**AGGREGATION, HYDROCARBON-CHAIN ORDER AND MOBILITY IN
THE SYSTEM OCTANOIC ACID—SODIUM OCTANOATE
A ^{13}C -NMR CHEMICAL SHIFT, NUCLEAR OVERHAUSER
ENHANCEMENT, SPIN—LATTICE RELAXATION AND ^1H -NMR
SELF-DIFFUSION STUDY**

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ABSTRACT

The present study uses ^{13}C -NMR chemical shifts, multifield ^{13}C relaxation and self-diffusion coefficients to study the two-component system sodium octanoate—octanoic acid. The shift and relaxation data strongly indicate the presence of sodium octanoate—octanoic acid complexes. ^{13}C -spin—lattice relaxation and nuclear Overhauser enhancement are used to characterize the hydrocarbon-chain order and mobility. A strong frequency-dependent relaxation is found. It is shown that the formation of complexes is governed by a very high equilibrium constant. Thus, it is valid to consider all sodium octanoate and octanoic acid as being present in the complexes. Although the molar ratio of sodium octanoate to octanoic acid and the aggregation number in the complexes cannot be determined, it can be concluded to be constant when the sodium-octanoate concentration is varied. The self-diffusion coefficient shows an accentuated decrease as sodium octanoate is added to octanoic acid. It is suggested that this is due to hydrogen bonding of octanoic acid to the complex.

INTRODUCTION

^{13}C nuclear magnetic resonance (NMR) has been used extensively in studies of surfactant systems such as ordinary and reversed micellar solutions [1, 2]. The chemical shift gives information on the CMC and aggregation numbers [3], while relaxation provides insight into alkyl-chain motions [4, 5]. Self-diffusion coefficients are very useful parameters in characterizing surfactant systems [6] and they can conveniently be determined by an NMR technique, namely the pulsed field-gradient spin-echo technique.

In what follows, we present a ^{13}C -NMR shift, ^{13}C relaxation and ^1H -self-diffusion study of the binary solution formed by sodium octanoate ($\text{C}_7\text{CO}_2\text{Na}$) and octanoic acid ($\text{C}_7\text{CO}_2\text{H}$). This system has been extensively studied by Ekwall and co-workers [7–11]. On the basis of viscosity, density and infrared spectroscopy, they proposed the existence of aggregates with the

composition 1 C_7CO_2Na /2 C_7CO_2H . The present study gives further evidence for the existence of complexes, although the study cannot determine either the C_7CO_2Na/C_7CO_2H molar ratio or the actual aggregation number of the complexes. The narrow ^{13}C -NMR signals, however, exclude the presence of extended aggregate structures.

Furthermore, the ^{13}C -relaxation data are interpreted in terms of a relaxation model developed by Wennerström et al. [12]. This analysis yields a time constant, τ_c^f , which is characteristic of the local alkyl-chain motions, and an "order parameter", S , which is characteristic of the anisotropy of the alkyl-chain motions. Finally, a time constant associated with motions of the whole complex is obtained.

It should be pointed out that the sodium octanoate—octanoic acid system is well suited for ^{13}C -NMR investigation since the rapid exchange at the carboxylic group ensures that the NMR signal from the acid and the salt coalesce, giving a good signal intensity and making the assignment of the spectrum quite simple.

EXPERIMENTAL SECTION

The ^{13}C -chemical-shift measurements were performed at 8.45 T with a Nicolet-360 spectrometer. The spectral width was 2500 Hz and the number of points was 8000, resulting in an optimal accuracy of ± 0.3 Hz. The shifts were determined relative to the methyl group, whose shift was found to be constant within experimental error. A capillary containing 2H_2O was placed concentrically in the NMR tube and was used to field-frequency lock the spectrometer. No susceptibility corrections were applied. The ^{13}C -spin—lattice relaxation times (T_1) were measured using the fast inversion-recovery technique (FIRT) at three different magnetic field strengths: 8.45 T with a Nicolet-360, 2.34 T with a Varian XL-100 and 1.40 T with a JEOL FX-60 spectrometer. Proton broad-band decoupling was used and, at the highest field, bilevel decoupling [13] was used to avoid heating. The nuclear Overhauser enhancement (NOE) was measured at the highest field with the dynamic nuclear Overhauser technique (DNOE). The relaxation times and the NOE were calculated from the experimental data by a three-parameter fit. The DNOE is a combined T_1 and NOE experiment and it gave values of T_1 in good agreement with those obtained from the FIRT (see Table 1). The self-diffusion coefficients were measured with the pulsed field-gradient technique of Stejskal and Tanner [14]. In this experiment, a Bruker 322S pulsed NMR spectrometer working at 90 MHz for protons with a home-built field-gradient unit was used. Details on how the self-diffusion coefficient is extracted from experimental data can be found in Ref. [15].

All measurements were performed at $27 \pm 1^\circ C$. The samples were prepared by weighing into glass ampoules that were subsequently flame-sealed. The samples were heated to $120^\circ C$ and then equilibrated at $25^\circ C$ for several days.

TABLE 1

A comparison of relaxation times from FIRT and DNOE experiments (numbering of carbons starts at the polar head group)

Sample composition NaC ₈ /HC ₈ (wt/wt)	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	Expt
0.26	0.327	0.427	0.509	0.627	0.904	1.336	2.48	FIRT
	0.319	0.426	0.507	0.627	0.873	1.325	2.44	DNOE
0.34	0.314	0.383	0.455	0.569	0.795	1.18	2.34	FIRT
	0.310	0.382	0.455	0.574	0.770	1.14	2.41	DNOE

RESULTS

The observed chemical shifts relative to the terminal methyl group are shown in Fig. 2 as a function of mole per cent sodium octanoate. Results are shown for two carbons, viz. numbers 2 and 3 (numbering starts at the polar headgroup).

Spin-lattice-relaxation rates, as a function of mole per cent sodium octanoate for carbons 2, 3 and 6 at three magnetic field strengths are given in Fig. 3. Finally, the self-diffusion coefficients as a function of mole per cent sodium octanoate are given in Fig. 4.

The error in the relaxation times was typically $\pm 10\%$ at the lowest field and $\pm 3\%$ at the highest field. The error in the diffusion coefficients is estimated to be $\pm 2.5\%$.

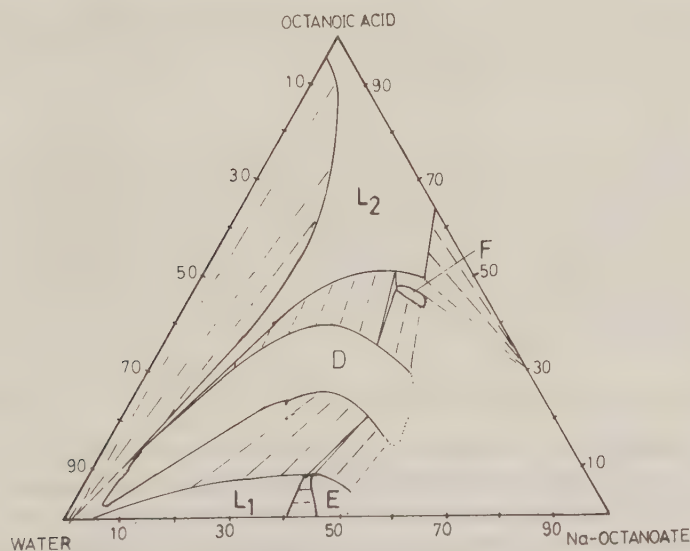


Fig. 1. The phase diagram of the system sodium octanoate-octanoic acid-water at 25°C (redrawn from Ref. [7]).

DISCUSSION

 ^{13}C chemical shift and relaxation

In general, for surfactant systems, each component is partitioned between the different environments comprising the system. In such a case, the NMR spectrum will be a weighted average over the different environments, provided that the molecules exchange sufficiently fast between these different environments.

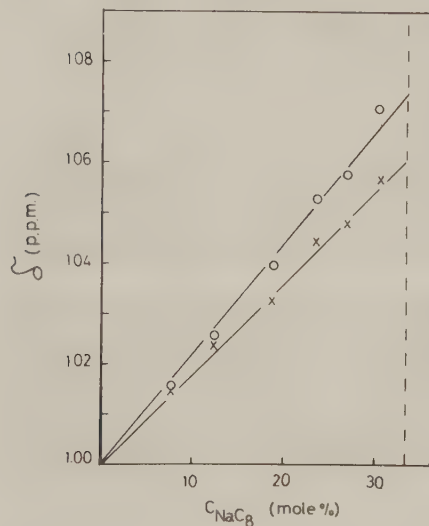


Fig. 2. Relative ^{13}C shifts for C_2 (○) and C_3 (×) as a function of sodium octanoate concentration. (---) indicates the phase boundary and (—) indicates the predicted behaviour according to Eqn (2) (see text, Discussion).

For the present system, it can be seen in Figs. 2 and 3 that both the chemical shift and the spin-lattice-relaxation rate vary linearly when $\text{C}_7\text{CO}_2\text{Na}$ is added to pure $\text{C}_7\text{CO}_2\text{H}$. We suggest that this is due to the presence of two different environments for the (from an NMR point of view) equivalent $\text{C}_7\text{CO}_2\text{Na}$ and $\text{C}_7\text{CO}_2\text{H}$ molecules. In line with the suggestions made by Ekwall and Solyom [8], the following model is proposed: assume that complexes are formed, viz.



Furthermore, let the equilibrium constant K for this reaction be very large and the ratio of a to b such that each added $\text{C}_7\text{CO}_2\text{Na}$ resides in a complex within the L_2 -region (see Fig. 1). Thus, the $\text{C}_7\text{CO}_2\text{Na}/\text{C}_7\text{CO}_2\text{H}$ system consists of complexes dissolved in an octanoic acid environment. Finally, assume that the chemical shift and the relaxation rate for the molecules

residing in the complex are different from those of the free molecules. Then

$$\Omega_{\text{obs}} = \frac{(a/b + 1) n_{\text{C}_7\text{CO}_2\text{Na}}^{\text{tot}}}{n_{\text{C}_7\text{CO}_2\text{Na}}^{\text{tot}} + n_{\text{C}_7\text{CO}_2\text{H}}^{\text{tot}}} \left(\Omega_{\text{complex}} - \Omega_{\text{free}} \right) + \Omega_{\text{free}} \quad (2)$$

where Ω is the chemical shift or relaxation rate, and n_i^{tot} is the total num-

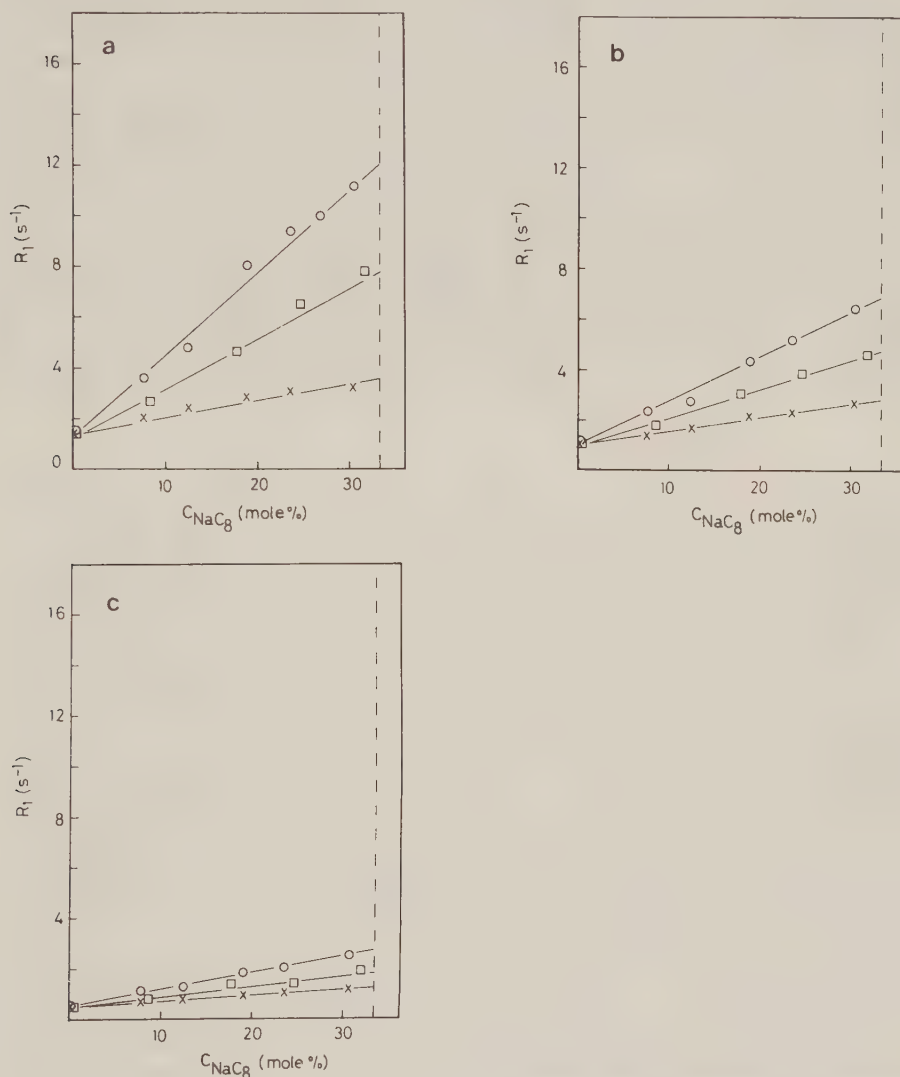


Fig. 3. ^{13}C -spin-lattice-relaxation rates as a function of sodium-octanoate concentration for three magnetic fields: ($\circ$), 1.40 T; ($\square$), 2.34 T; ($\times$), 8.45 T. (a) Results for C_2 ; (b) results for C_3 ; (c) results for C_6 . (---) and (—) have the same meaning as in Fig. 2.

ber of moles of component i , Ω^{complex} and Ω^{free} are the values of the NMR parameters for the molecules "bound" in complex and for the molecules "free" in the octanoic acid environment, respectively.

Equation (2) predicts a linear variation of the chemical shift and the relaxation rate as the amount of $\text{C}_7\text{CO}_2\text{Na}$ is increased, as long as all the molecules are not in the "all-bound" state. It should also be pointed out that the shift data itself is not enough to verify the presence of aggregates. The linear shift variation could merely be interpreted as the result of forming a molecular dispersed mixture of two components. However, this is contradicted by the frequency-dependent relaxation data, which strongly suggest the presence of some aggregated structure. The conformity of the experimental data with the prediction of Eqn (2) can be seen in Figs. 2 and 3. Since the chemical shifts or relaxation rate of the complex cannot be extracted from the experimental data, it is not possible to determine $(a + b)$, much less a and b individually. As noted earlier, there is substantial experimental evidence that the molar ratio of $\text{C}_7\text{CO}_2\text{H}$ to $\text{C}_7\text{CO}_2\text{Na}$ is 2:1 in the complexes. The strongest experimental evidence for this molar ratio is probably provided by the IR investigation by Friberg et al. [10]. They observed a linear decrease in the out-of-plane deformation vibration of the OH group at 950 cm^{-1} when sodium octanoate was added. At the phase

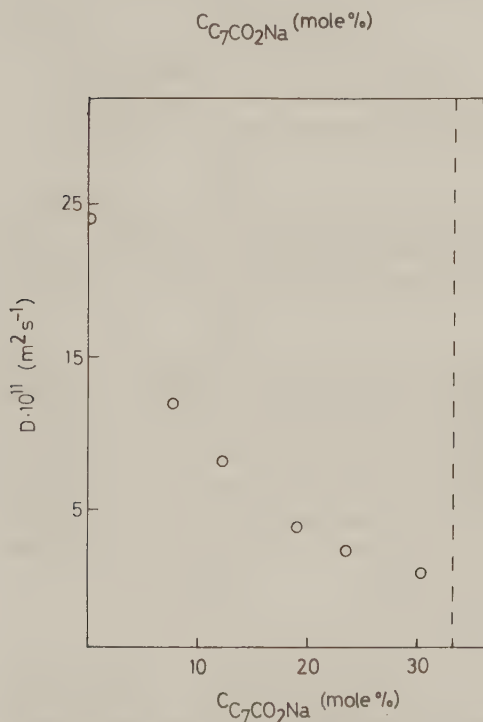


Fig. 4. The self-diffusion coefficient as a function of mol% sodium octanoate in octanoic acid.

boundary (see Fig. 1) the signal was totally absent. Thus, all octanoic acid was consumed at this point. Therefore, it is sound to assume that the chemical shifts and relaxation rates at the phase boundary represent an "all-bound" state, i.e., Ω^{complex} in Eqn (2). Values for the different NMR parameters for the complex can be found in Table 2.

TABLE 2

Values of the relaxation rates and the chemical shifts for pure octanoic acid and the complex

Carbon number	Relaxation rates (s^{-1})				Chemical shifts (ppm)	
	Complex			Free	Complex	Free
	1.40 T	2.35 T	8.45 T			
2	12.05	7.75	3.20	1.43	21.68	20.21
3	6.82	4.75	2.78	1.07	11.56	10.92
4	5.20	3.32	2.32	0.80	15.68	15.37
5	4.10	2.50	1.78	0.82	15.42	15.37
6	2.70	1.90	1.06	0.63	18.09	18.06
7	1.66	1.25	0.85	0.46	8.90	8.90
8	0.34	0.31	0.27	0.22	0.0	0.0

Interpretation of the ^{13}C -relaxation data

We now turn to the interpretation of the relaxation data. As stated above, there is a clear frequency dependence in T_1 as NaC_8 is added to HC_8 . The frequency dependence is largest for the carbon next to the carboxylic head group, and decreases towards the methyl group. This indicates the presence of slower motions that contribute to the relaxation and which, furthermore, contribute most for the carbons close to the head group. These motions must have correlation times, τ_c , such that $\omega_c \tau_c$ or $(\omega_c \pm \omega_H) \tau_c \sim 1$, where ω_c and ω_H are the ^{13}C - and ^1H -resonance frequencies, in angular frequency units. This means that the motions must have time scales which fall approximately in the nanosecond region. A rather obvious candidate for these motions is the tumbling of the complex itself. In order to proceed further and analyse the relaxation data, one needs a model for the relaxation. Such a model has been presented by Wennerström et al. [12]. The basis for this model is a separation of the motions giving relaxation, into fast local motions and slower motions associated with the motion of the aggregate itself. As discussed above, analysis of the relaxation data gives three parameters: τ_c^f , τ_c^s and S . τ_c^f and τ_c^s are the correlation times for the fast and slow motions, respectively, while S is the (local) order parameter which is characteristic of the anisotropy of the local motions that the C—H vectors undergo. A detailed derivation of the relaxation equations as well as discussions on how to evaluate these three parameters

from the experimental relaxation data can be found elsewhere [12, 16]. We merely state the result of such an analysis here.

Using data from Table 2, we have deduced the correlation time for the fast local motions and the order parameters for the alkyl chain in the complex. These are presented in Figs. 5a and 5b. The value of τ_c^f falls around 20 ps, indicating that the local motions of the alkyl chains are quite rapid. Indeed, this value is in good agreement with the correlation times obtained from octanoic acid (Table 3) and with those that can be calculated from ^{13}C T_1 -data for n-alkanes [17, 18]. The anisotropy of these motions, as described by the parameter S , is largest close to the head group and decreases in an almost linear fashion towards the terminal methyl group. The values of S for the carbons close to the polar group are quite large compared with typical values found in other phases in the NaC_8/HC_8 system when water is added [19]. This indicates that the amplitude of the motions these carbons undergo is comparably small. Thus, the head groups of the molecules in the complexes are rigidly held together, while there is considerable freedom of motion closer to the terminal methyl group. This result is in

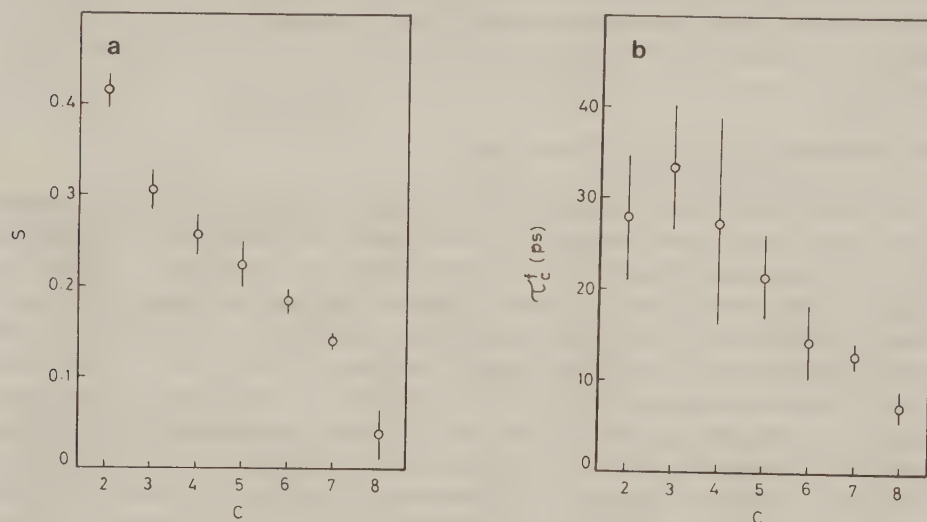


Fig. 5. Order parameters (a) and fast correlation times (b) for the alkyl chains in the complex. The error bars correspond to an approximately 80% level of confidence.

TABLE 3

Fast correlation times of octanoic acid, calculated according to the formula $R_1 = 4.293 \times 10^{10} \tau_c$

Carbon number	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
$\tau_c^f \times 10^{11}$ s	3.3	2.2	2.1	1.91	1.46	1.07	0.51

good agreement with the proton-NMR study presented in Ref. [10]. Finally, the correlation time for the slow motion, associated with tumbling of the complex, is 1.7 ns, roughly the same as that obtained for a C_7CO_2Na ordinary micelle [19].

As noted above, the spin-lattice-relaxation rate is determined mainly by motions with correlation times such that $\tau_c \lesssim 1/\omega_0$. It is therefore rather insensitive to slow motions. On the other hand, the line-width, i.e., the spin-spin-relaxation rate [12], depends strongly on slow motions. Thus, the presence of any long-lived extended structures in the present case would give rise to broad lines in the ^{13}C spectrum. The line-width for the α -carbon at 30 mol% C_7CO_2Na is 5.1 Hz at 1.4 T. If we estimate the contribution from magnetic-field inhomogeneity and insufficiently decoupled proton couplings to be 1 Hz, the true line-width is 4.1 Hz and consequently, T_2 is 78 ms. This is to be compared with T_1 at the same field, which is 88 ms.

Although it is difficult to measure the true ^{13}C line-width accurately, due to difficulties in estimating the contributions from field inhomogeneity and unresolved J -couplings, it is evident that the spin-spin-relaxation rate is only slightly greater than the spin-lattice-relaxation rate. This finding excludes the presence of any long-lived, extended structures in the water-free part of the L_2 -region in the C_7CO_2Na/C_7CO_2H system.

Interpretation of the self-diffusion coefficients

As can be seen in Fig. 4, it is evident that the self-diffusion data do not follow the same pattern as do the ^{13}C shifts and relaxation rates, upon addition of C_7CO_2Na to pure C_7CO_2H . Since Eqn (2) is, in principle, equally valid for self-diffusion coefficients, we would expect, at least for low-volume fractions of complex where obstruction effects [14] are less important, a linear dependence of D on the added amount of C_7CO_2Na . Furthermore, letting (a/b) equal 2 and taking the values for D measured for pure C_7CO_2H and at 8 mol% C_7CO_2Na , Eqn (2) predicts a negative D^{complex} . Thus, it appears that the self-diffusion data alone are not compatible with a 2:1 complex. In what follows, we will give a tentative explanation for this apparent inconsistency.

Consider Fig. 6, where we visualize the possibility of further C_7COOH molecules associating with, for example, the 2 C_7COOH and 1 C_7CO_2Na complex, through hydrogen bonding. In other words, we have an "inner" complex consisting of three molecules and an outer "layer" consisting of more loosely associated octanoic-acid molecules. The point now is that only in the diffusion experiment do these loosely attached molecules contribute to the fraction bound molecules. The reasons for this are as follows. For the IR and ^{13}C -shift experiments, the properties of the loosely attached molecules are very different from those of the inner complex, the former resembling those of the octanoic-acid dimer. For the relaxation-time measurements, the lifetime of the molecules in the outer layer is

shorter than the rotational correlation time of the complex. Thus, as far as the relaxation times are concerned, these molecules are considered as free. (This is why we designate only the inner molecules as a complex, the criterion being that the complex should exist for at least the time it takes for it to make a full rotation.) Finally, since the diffusion measurement monitors mass transport over a time that is of the order of a tenth of a second, it is clear that in this case the outer layer of molecules does contribute to the fraction bound in Eqn (2). As the sodium-octanoate fraction is increased, the supply of octanoic acid decreases and less molecules can associate with the complex. Thus, the decrease in the self-diffusion coefficient levels off towards the phase boundary (see Fig. 4).

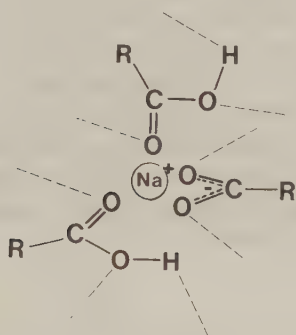


Fig. 6. A visualization of the possibility of further octanoic acid association to the complex $2 \text{ C}_7\text{COOH}/\text{C}_7\text{CO}_2\text{Na}$.

CONCLUSIONS

The ^{13}C data presented here support the notion that a complex with a molar ratio of 2:1 of octanoic acid to sodium octanoate is formed in the one-phase area of this binary system.

^{13}C -relaxation data indicate that the local motions which the alkyl chains undergo in these complexes are quite rapid. Furthermore, these motions appear to be rather restricted near the carboxylic head group, but this restriction decreases near the terminal methyl group.

The self-diffusion data at low sodium-octanoate concentrations are inconsistent with the two-site model. However, this discrepancy can be explained by considering a situation where additional octanoic-acid molecules are hydrogen bonded to the complex. This "third" site is indistinguishable from the "free" acid site in the ^{13}C -NMR and IR measurements.

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IV

SURFACTANT ALKYL CHAIN ORDER IN THE ANISOTROPIC AND
ISOTROPIC PHASES OF THE SYSTEM SODIUM OCTANOATE ,
OCTANOIC ACID AND WATER

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ABSTRACT

Quadrupolar splittings of ^2H are used to obtain order parameter values of α - and per-deuterated octanoic acid in the liquid crystalline phases of the system sodium octanoate-octanoic acid-water. The order parameter profiles in the mesomorphic phases are compared with those obtained from frequency dependent ^{13}C -NMR relaxation studies in the isotropic solution phases L1 and L2. The order parameter profiles are shown to exhibit characteristic shapes in each phase and the order parameter values are observed to vary within the L1, L2 and D phases.

A general observation is that the order parameters of the methylene groups close to the polar head are sensitive to the water concentration. In the L1, L2 and D phases the order parameters decreased with increasing water concentration. Furthermore, at constant water concentration (ca. 50w%) the α -carbon order parameter decrease in the sequence $\text{L1} \approx \text{E} > \text{D} > \text{L2}$. The α -carbon order parameter is also found to decrease at constant water concentration if the fraction octanoic acid is increased.

All these observations indicate that there is no simple explanation to the observed order parameter changes.

INTRODUCTION

Surfactant chain order in liquid crystalline phases(1-4) has been extensively studied by ^2H -NMR. Effects of various variables such as temperature, chain length,

functional groups and solubilisation of alcohols, proteins and cholesterol have been studied(5-7). Along with these and other experimental findings several theoretical models have been developed and applied to describe the surfactant alkyl chain order(8-12).

The order parameter values do not contain any information on the mobility of the chains but inform about the amplitude and direction of the motions involved(13). Order parameter profiles for the surfactant alkyl chain in the micellar phases L1 and L2 were determined from frequency dependent ^{13}C -NMR spin-lattice relaxation studies using a two-step relaxation model(14). The results are published in recent papers(15-17).

In this study we will report the order parameter values for all phases in the system sodium octanoate-octanoic acid-water. The aim is to provide experimental results for testing theoretical packing models of hydrocarbon chains. We will also briefly discuss the relation between aggregate structure and order parameter profiles and propose some explanations for the observed changes in the α -carbon order parameter values.

The advantage of the present system is that the influence of aggregate structure on the order parameter profile in several phases, like L1, L2, D, E and F, can be examined. Furthermore, these structures are well characterized using other methods like x-ray low angle diffraction.

EXPERIMENTAL SECTION

The chemicals used were sodium octanoate and octanoic acid (biochem. grade) from BDH Chemicals Ltd. The per-deuterated octanoic acid (90% deuterated) was from Larodan Fine Chemicals. α -deuterated sodium octanoate was obtained by heating a mixture of sodium octanoate, D₂O and NaOD, with a molar ratio of D₂O to sodium octanoate equal to 20, to 160°C in sealed glass ampoules. The glass ampoules were then kept at this temperature for approximately a week under occasional shaking. The sodium octanoate was then recovered after dissolving the mixture in methanol, filtering and evaporation of the methanol.

The samples were prepared by weighing appropriate amounts of the chemicals into glass ampoules which were then flame-sealed. The samples were heated to 120°C and thereafter kept at 25°C for several days before the measurements to ensure equilibrium conditions.

The samples were examined between crossed polarizers and found to consist of a single phase after this period of time.

The ²H-NMR spectra were obtained on a Nicolet-NM360 spectrometer. A one-pulse sequence was used and typical parameter settings were 20 μ s pulse width (90° pulse), 500 ms pulse repetition time, 32 K data points, 124 kHz spectral width and 2000- 6000 accumulations with quadrature detection. Most of the data from the lamellar D-phase were obtained on a home-built Supercon- 250 spectrometer.

Typical parameter settings were 10000-120000 accumulations, 12 K data points, 120 kHz spectral width and a pulse width of 15 μ s and quadrature detection.

THEORETICAL CONSIDERATIONS

Deuterium, being a spin = 1 nucleus, has a quadrupolar moment which interacts with the electric field gradient at the nucleus. This gives rise to quadrupolar splittings in anisotropic phases. For the case of a cylindrically symmetric electric field gradient, the splitting of the two peaks in the ^2H - NMR spectrum of a polycrystalline sample is given by

$$\Delta = 3/4 (e^2 q Q / h) |S| \quad (1)$$

where $e^2 q Q / h$ is the quadrupole coupling constant, given the value 167 kHz(18) in the present work, and S is the order parameter defined as

$$S = 1/2 (3 \langle \cos \theta_{MD} \rangle - 1) \quad (2)$$

where θ_{MD} is the angle between the principal axis of the field gradient symmetry axis and the local director.

It is convenient to refer order parameters measured in different phase structures to the normal of the aggregates in order to facilitate comparison between the different phases. Calling this order parameter S we obtain for rodshaped micelles(13)

$$S = - 2 S_{\text{obs}} \quad (3)$$

and for lamellar structures

$$S = S_{obs} \quad (4)$$

The order parameters between the lamellar and the isotropic L1 and L2 solutions are directly comparable.

Because of the fast exchange of counterion common NMR signals are obtained from the acid and the salt. This will complicate the analysis of the data since a weighted average order parameter is then observed.

RESULTS

The slightly modified (B and C phases have been omitted) phase diagram for the system sodium octanoate - octanoic acid - water (from ref.19) is shown in figure 1.

The compositions studied are indicated by dots in the phase diagram and given in table 1. Concentrations for the C13-NMR data

are separately given in the figure legends.

Table 1. Compositions studied in the system sodium octanoate - octanoic acid - water

sample		weight %		
number	sodium octanoate	octanoic acid	water	

per deuterated samples

E-phase	42.5	8.7	48.8	
F-phase	40.5	45.4	14.1	

D-phase

1	32.4	40.2	27.4
2	12.4	23.9	63.7
3	21.4	35.8	42.8
4	30.9	28.0	41.1
5	31.6	29.7	38.7
6	35.7	32.2	32.1
7	36.4	34.0	29.6
8	37.6	36.3	26.1
9	53.7	23.5	22.7
10	50.2	23.6	26.2
11	47.5	21.6	30.9
12	46.5	19.7	33.8

a-deuterated samples

13	12.2	22.2	65.6
14	15.8	28.3	55.9
15	20.1	35.4	44.5
16	24.7	30.0	45.3
17	27.2	32.7	40.1
18	28.9	35.4	35.7
19	41.2	27.8	31.0
20	37.9	32.4	29.7
21	34.6	34.6	30.8
22	32.7	27.7	39.6
23	35.5	29.4	35.1
24	15.8	29.0	55.2
25	48.0	21.9	29.4

In figure 2, a typical ^2H -NMR spectrum of the inverted hexagonal F-phase is shown. The order parameter values are deduced from the spectrum assuming decreasing order along the chain towards the terminal methyl group. Studies(24) on selectively deuterated compounds and comparison with results from ^{13}C -NMR (15,16,17) show that this assumption is justified. In this study we have also performed ^2H -NMR experiments with α -deuterated octanoate in the lamellar D-phase.

DISCUSSION

This discussion has been divided into two parts. First, we will treat the variations of the order parameter profile in the various phases and then compare the profiles between the these phases.

The Lamellar D-phase

There is a large change in the order parameters in different parts of the lamellar phase as shown in figure 3. The largest changes are in the water poor part and in the water rich part only a slight decrease is seen when water is added.

From the α -carbon order parameter data iso-order parameter lines were constructed. These are shown in figure 4.

The order parameters for the carbons close to the head group have been suggested to be inversely proportional to the head group area²⁰. The results in figure 4, would then indicate that the head group area increases when increasing the water content. From X-ray studies, it is possible to calculate the thickness of the lamellae. In figure 5. the lamellae thickness as a function of water concentration is shown. We see an initial decrease in the lamellae thickness when water is added. This indicates that the head group area is increasing. This will increase the conformational freedom of the alkyl chain which is seen as a decrease in the order parameter.

At constant water concentration the α -carbon order parameter values decrease at increasing octanoic acid content as seen in figure 6.

If the octanoic acid and the sodium octanoate molecules have different order parameters we will observe a weighted average order parameter and then

$$S^{OBS} = P(S^O - S^N) + S^N$$

where S^O is the octanoic acid and S^N is the sodium octanoate order parameters respectively. P is the octanoic acid fraction. As seen in figure 6, curved lines are obtained which indicate that the problem is complex. Extrapolation of the lines in fig. 6, indicate that the sodium octanoate order parameter decrease with added water. Changing the fraction octanoic acid to sodium octanoate will alter the electrostatic interactions between the octanoate head

groups. At low water concentrations incomplete hydration of the head groups will probably also influence the observed order parameter.

It has been suggested(21) that above ca. 40 w% water, the lamellae thickness is not changing any more and that all additional water goes to the water layer. However, the order parameter is still decreasing with added water. The decrease is less accentuated and it is possible that an increased amount of monomers in the water layer would reduce the observed total order parameter(24).

The Isotropic L1 and L2 Phases

The order parameter profiles for the surfactant aggregated in the isotropic L1 and L2 phases as obtained from field dependent ^{13}C -NMR spin-lattice relaxation measurements have been discussed in earlier publications(15,16). They are included here for comparison together with the profile found for the (2/1) sodium octanoate/octanoic acid complex(17) formed in the water free region of the L2 phase (figure 7a-c).

As a general observation we find that the order parameters decrease within each phase as the water concentration is increased (figure 8). The order parameter change in the L1-phase is probably due to the decreasing electrostatic interaction between the head groups as the sodium octanoate concentration is increased and this leads to a decreasing head group area (the aggregation number grows slightly). The order parameter is lowered at increased

repulsion between the head groups, since more space is available.

In the L2-phase the initial introduction of water to the water-free complex drastically lowers the order. At least initially the hydration of the head groups will lower the order. At high water concentration in the L2 phase the order parameter values resemble those found for normal micelles (see fig. 7 a,b).

Comparison of the Order in the Anisotropic Phases

The order parameter profiles for the various mesomorphic phases are compared in figure 3.

The difference in order parameter profiles indicate the chain packing is different in the various aggregate structures. Also, (cf. fig. 5) X-ray measurements indicate that the alkyl chains in the inverted hexagonal phase have shorter mean lengths than in the lamellar phase. Thus, lower order parameters in the F-phase are consistent with X-ray data.

In general, longer chain surfactants (C12 - C18), cationic and anionic, show order parameter values of 0.3 and less. The profile is rather invariant to aggregate structure and usually a characteristic "plateau" is seen(23). In the nonpolar end of the surfactant hydrocarbon chain the order parameter values decrease rapidly. In the present study, C7COONa, experimental results show that the order parameter profile is sensitive to aggregate structure

(figures 3 and 7). This is a consequence of the short alkyl chain and the different packing conditions imposed by the aggregate structures.

At constant water concentration (ca. 50 w%) the highest order is found for hexagonal rods and micelles, lower for the D phase and lowest for the L2 phase. This can be explained by the increased fraction of octanoic acid if the acid has a lower order parameter than the octanoate.

The low order for the F-phase is a bit unexpected but this is probably due to the presence of free octanoic acid.

ACKNOWLEDGEMENTS

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FIGURE CAPTION

Figure 1. A schematic phase diagram of the system sodium octanoate-octanoic

acid-water. The compositions studied are indicated with dots.

Figure. 2. ^2H -NMR spectrum of inverted hexagonal phase F.

Figure. 3. Order parameter profiles for the mesomorphic phases E, F and D at 27 C. The symbols for the D-phase denote the following samples: (filled circle) sample 1, (open circle) sample 2, (star) sample 3.

Figure 4. Iso-order parameter lines for the α -carbon in the lamellar phase.

Figure. 5. Lamellae thickness and rod diameters as obtained from X-ray experiments at 20 C. Data is taken from reference 21. The lines indicate dilution lines at constant octanoic acid to octanoate ratios, filled squares .32, filled circles .48, filled triangles .64 and open squares .53 .

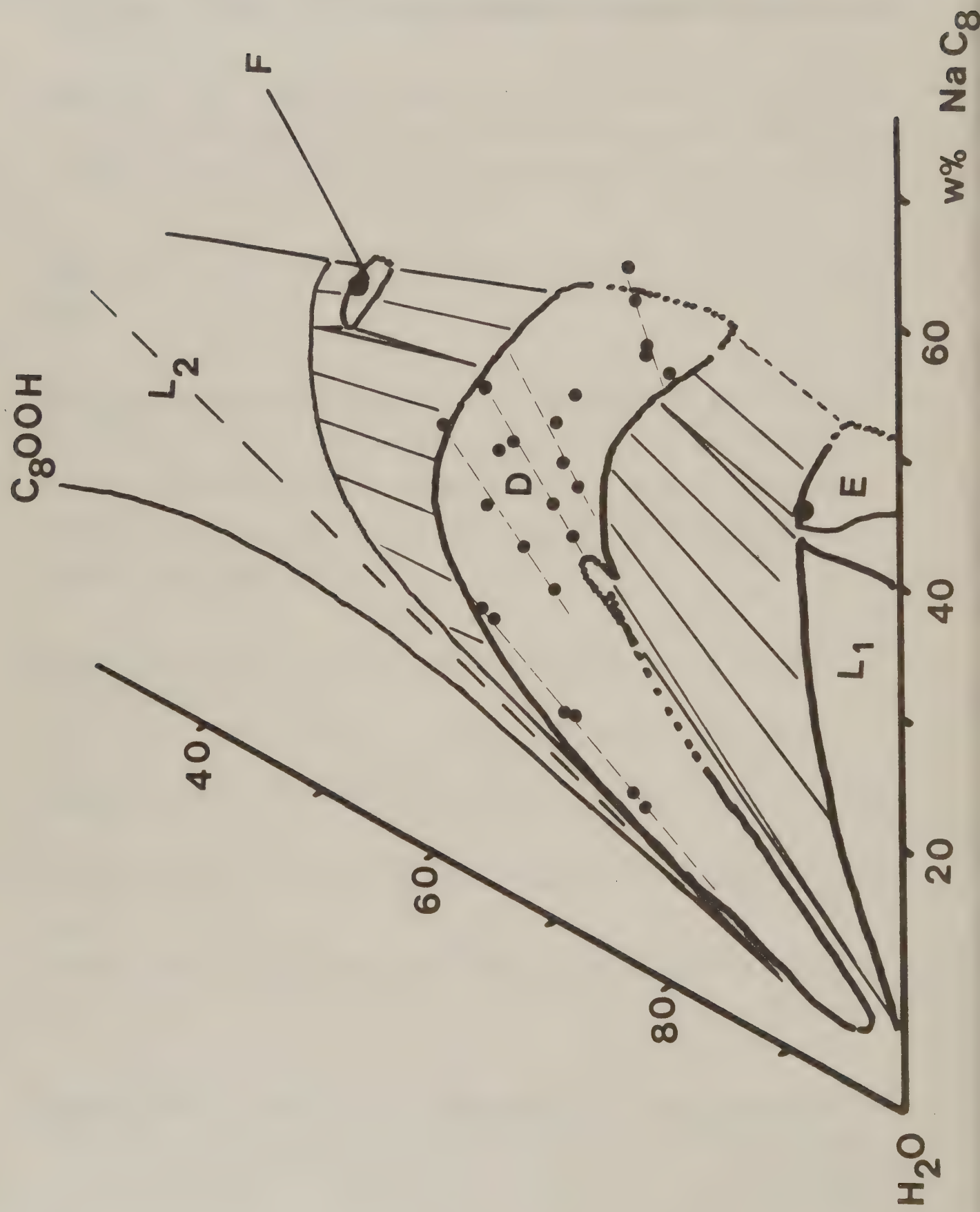
Figure 6. α -carbon order parameters as a function of octanoic acid fraction.

Figure. 7 . Order parameter profiles for the aggregates in a) the L1 and
b) the L2 phase and in c) the water free part of the L2 phase. All these
profiles are extracted from C-13 NMR relaxation data (from ref.16 and 17)

Figure 8. Water concentration dependence for the α -carbon in the

various phases. Filled triangles are results of per-deuterated samples and open squares are results of a-deuterated samples in the **D phase**

FIGURE 1.



H-2 SPL. F-PHASE
 SYTEMET NAC8-C800H-H2O
 SW=66000HZ 1-PULS

FIGURE 2.

ONE-PULSE SEQUENCE

P2= 20.00 USEC
 D5= 500.00 MSEC
 NA= 1000
 SIZ= 327.6
 AI= 181.07 MSEC
 CPD ON= 1 ARC ON
 BUTTERWORTH ON
 OR ATT= 8
 ADC= 8 BITS AI= 8
 SW= +/- 62500.0 DM= 8 USEC
 RG= 10 USEC DE= 8 USEC
 TL-HIGH POWER ON
 F2= 961.790581
 BB MODULATION ON
 OF= 1740.72
 SF= 55.538594
 EM= 10.00
 PA= .9
 PR= -352.0
 T(C)= 28
 SCALE= 870.89 HZ/CM
 15.6814 PPM/CM

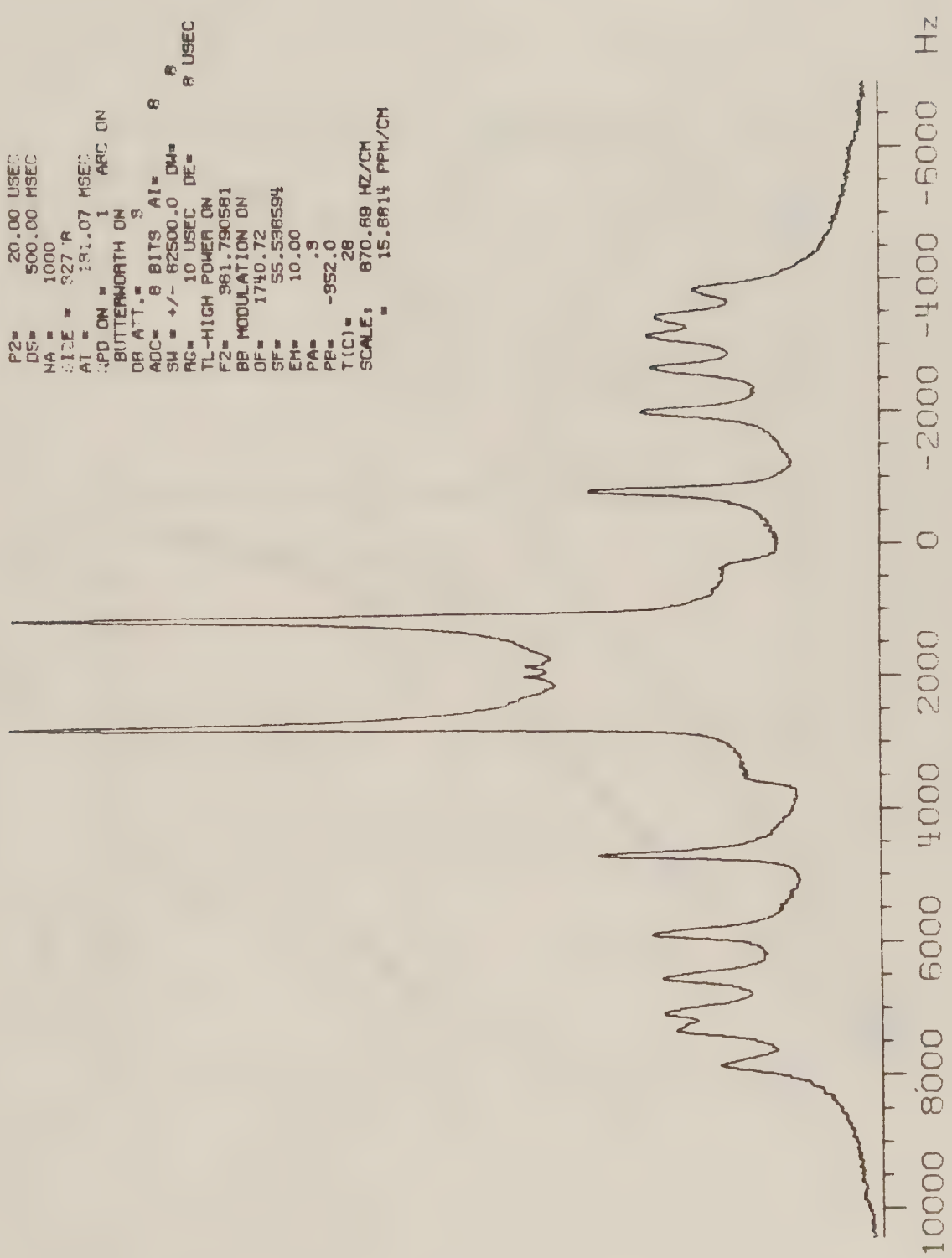


FIGURE 3.

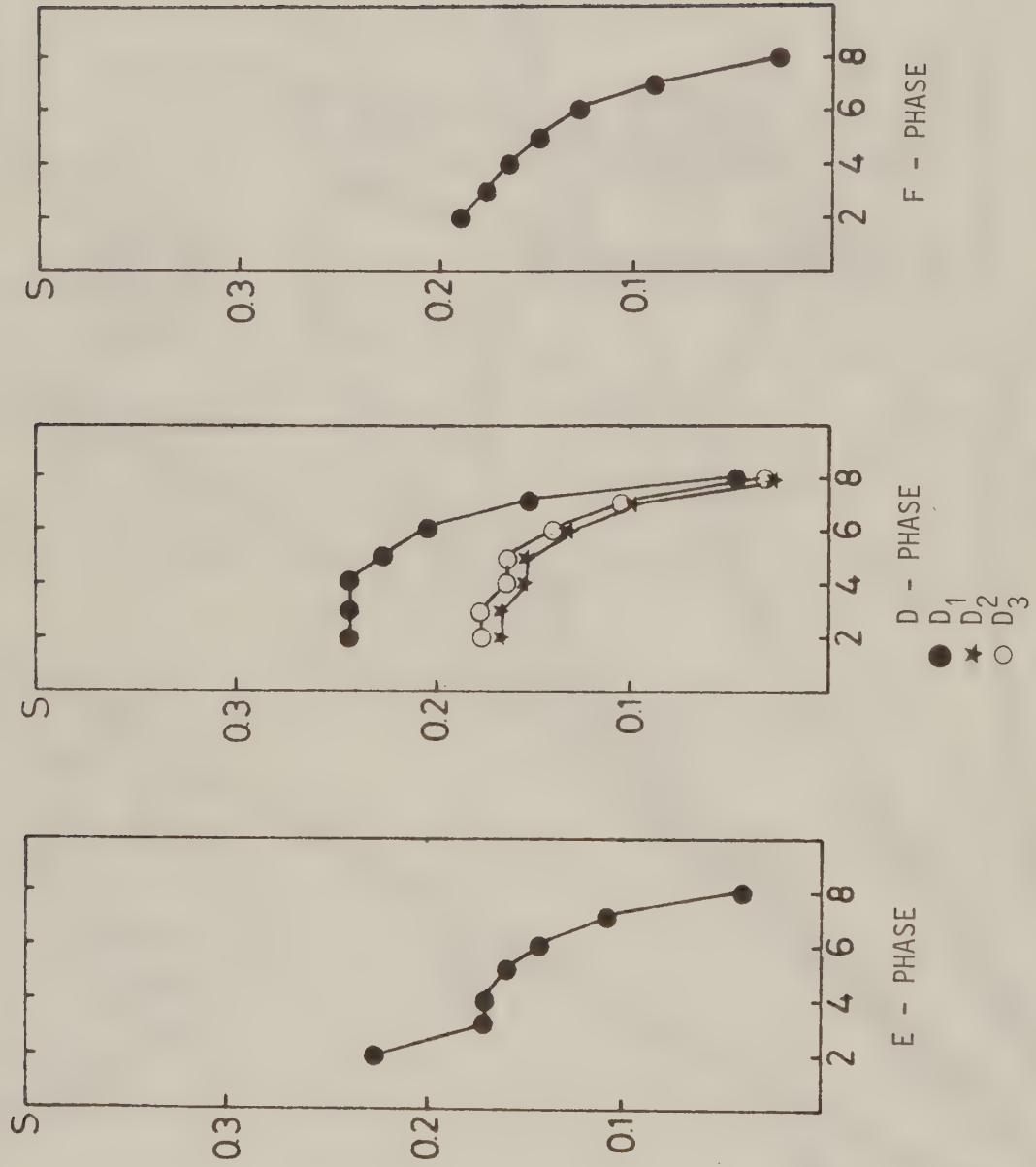


FIGURE 4,

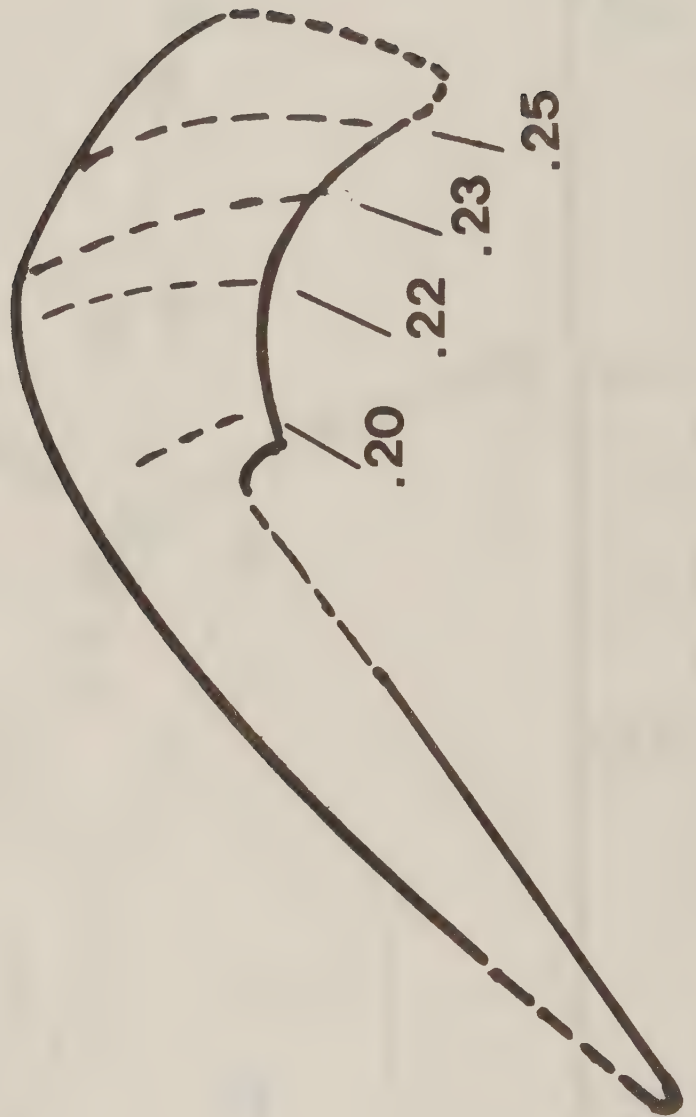


FIGURE 5.

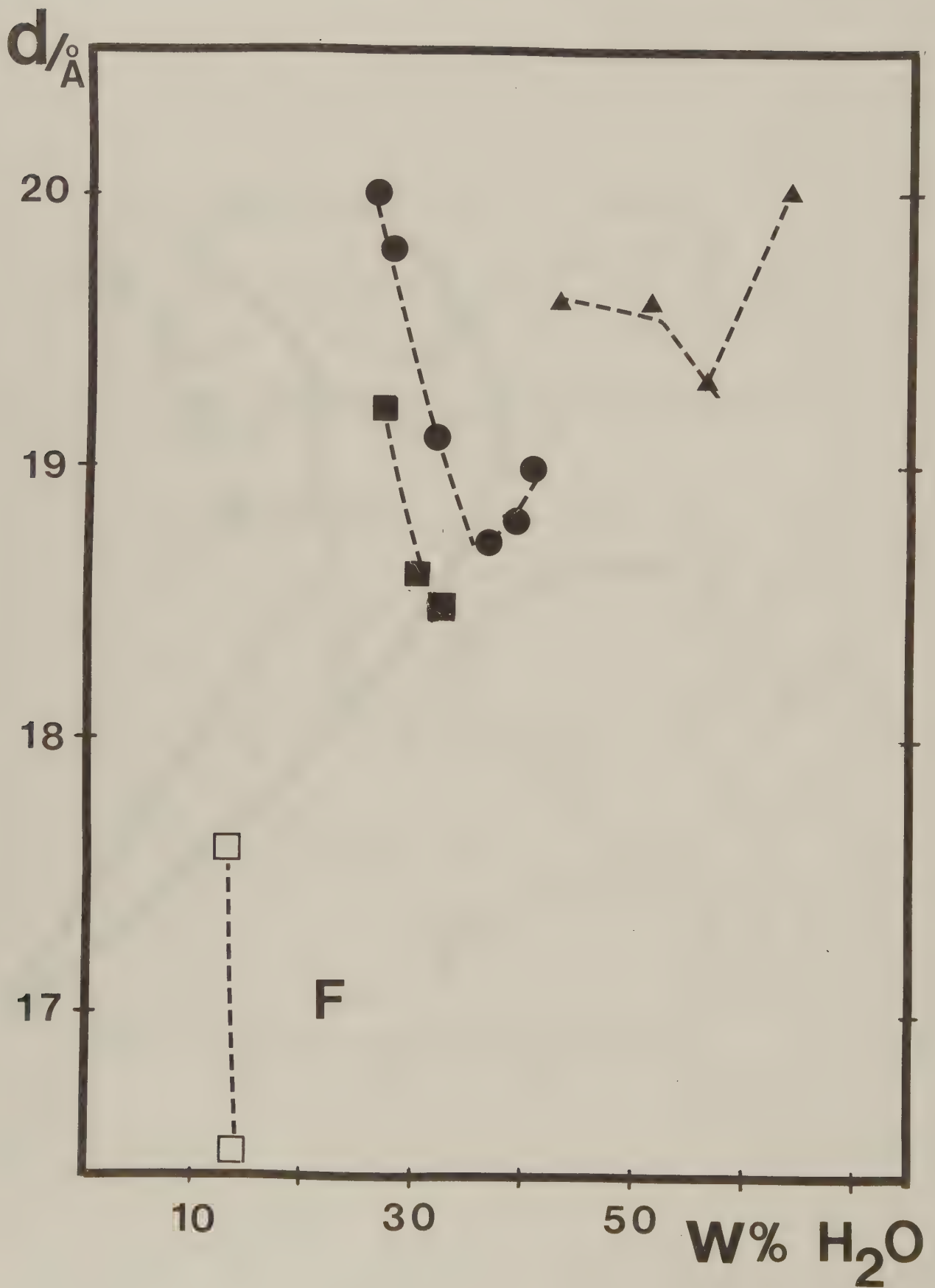


FIGURE 6.

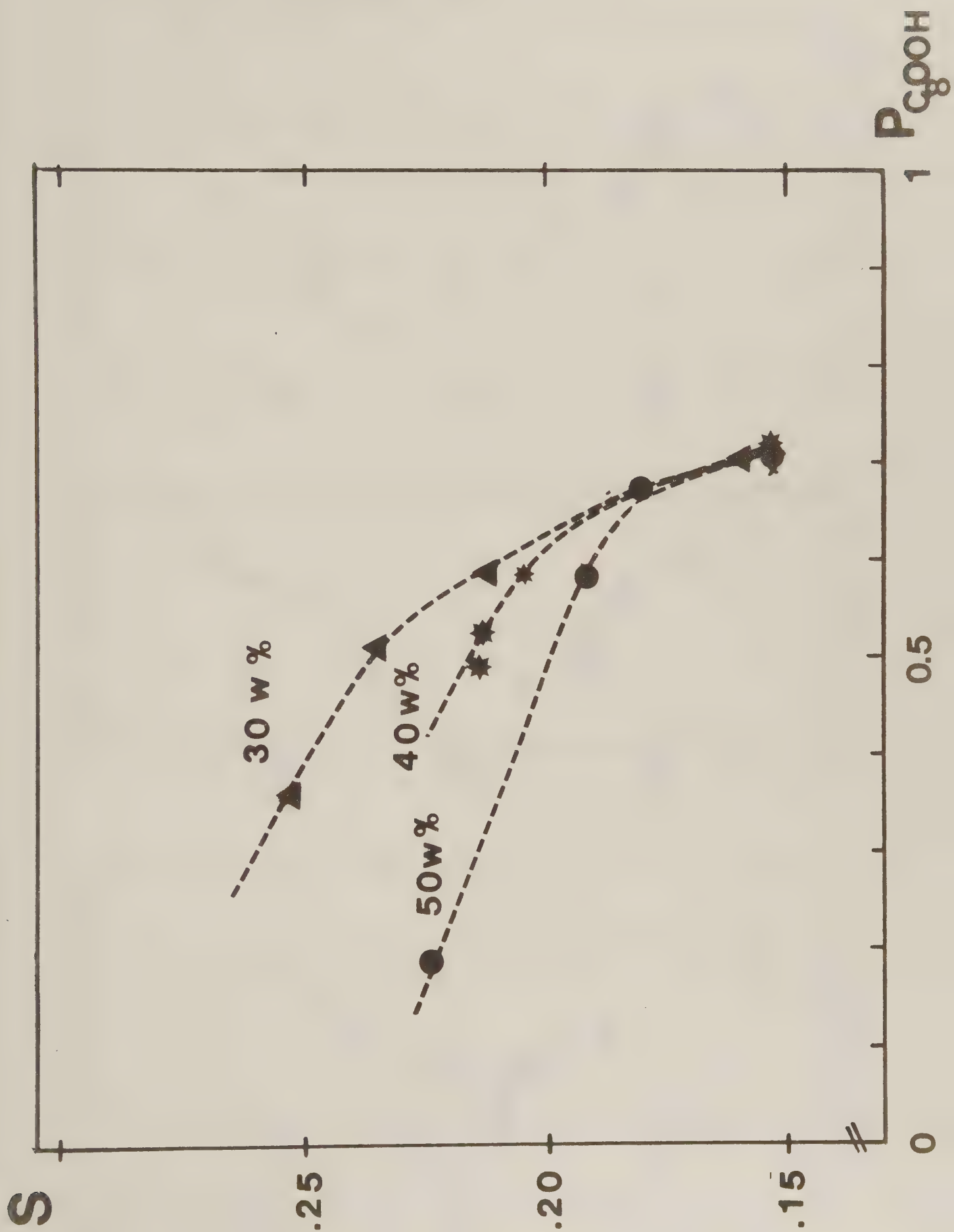


FIGURE 7 a)

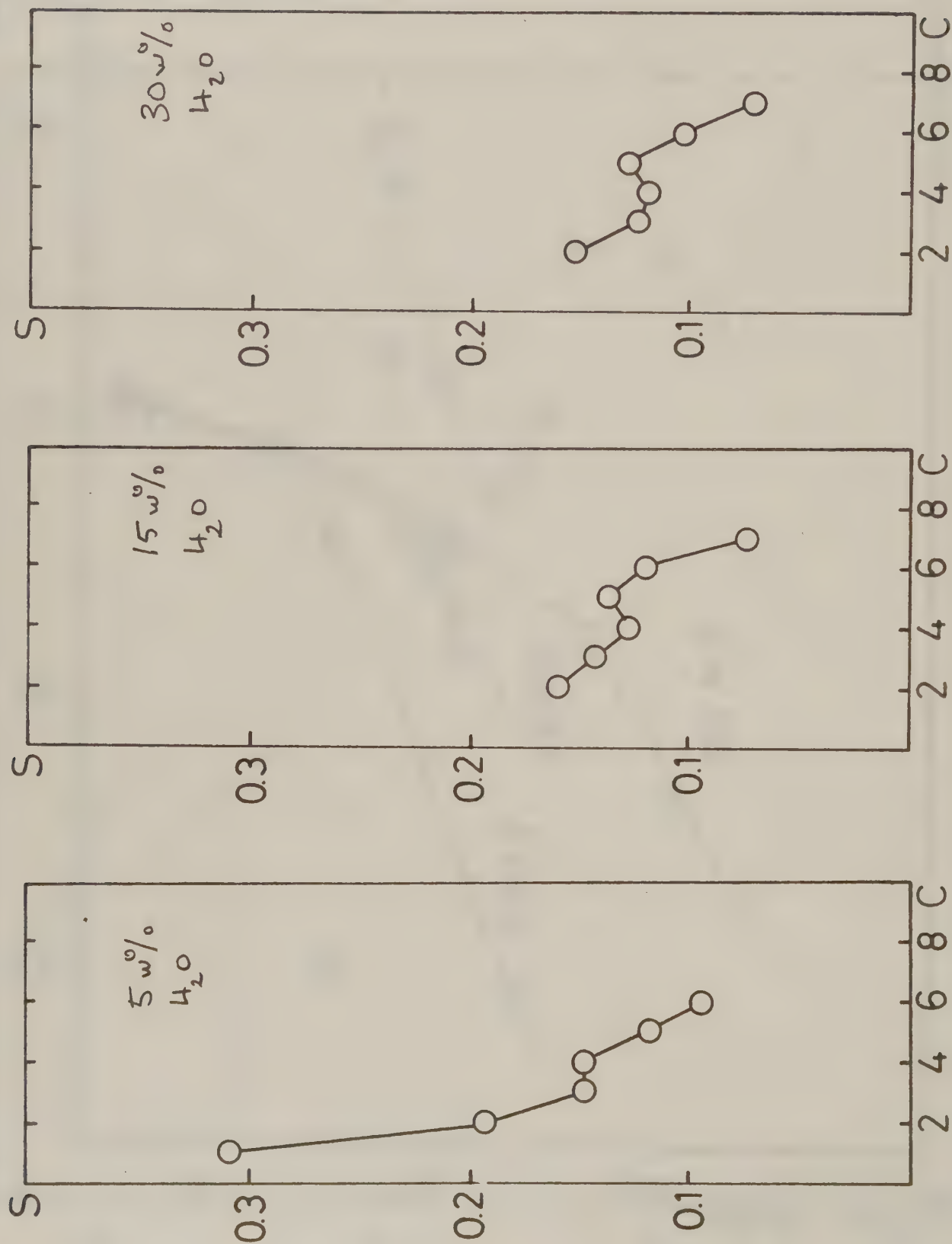


FIGURE 7 b)

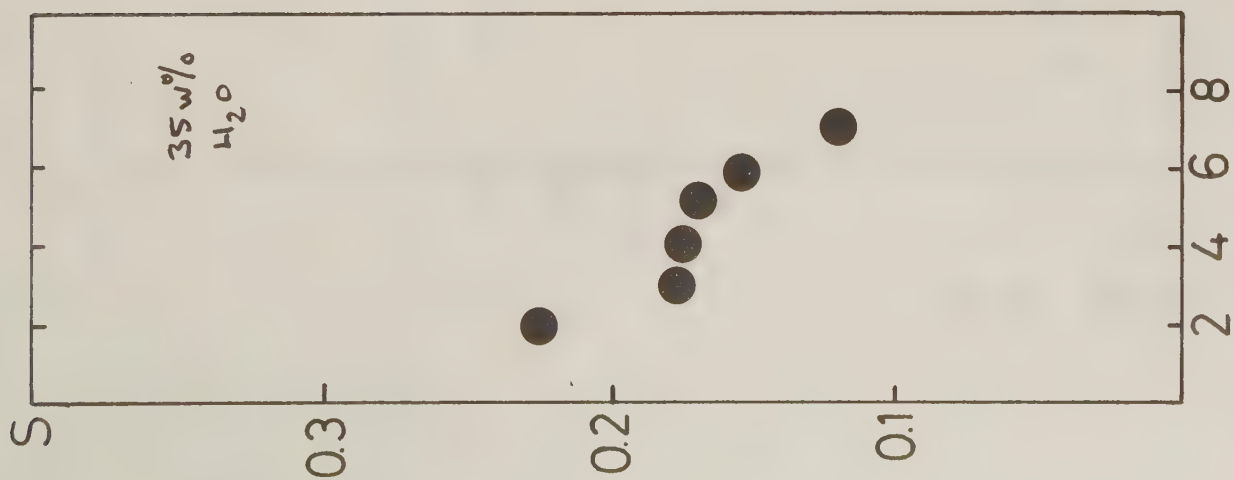
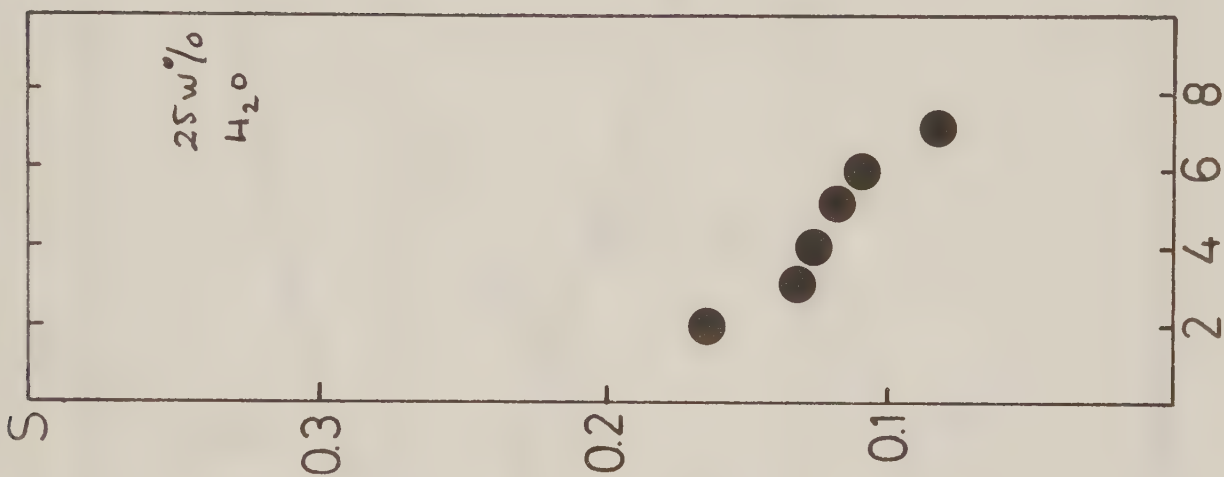
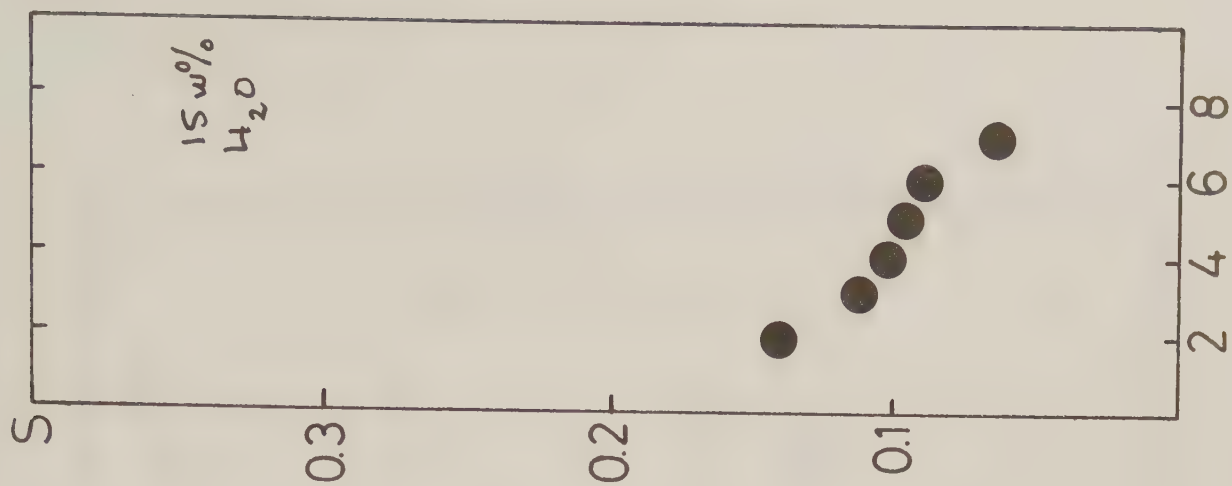


FIGURE 7c)

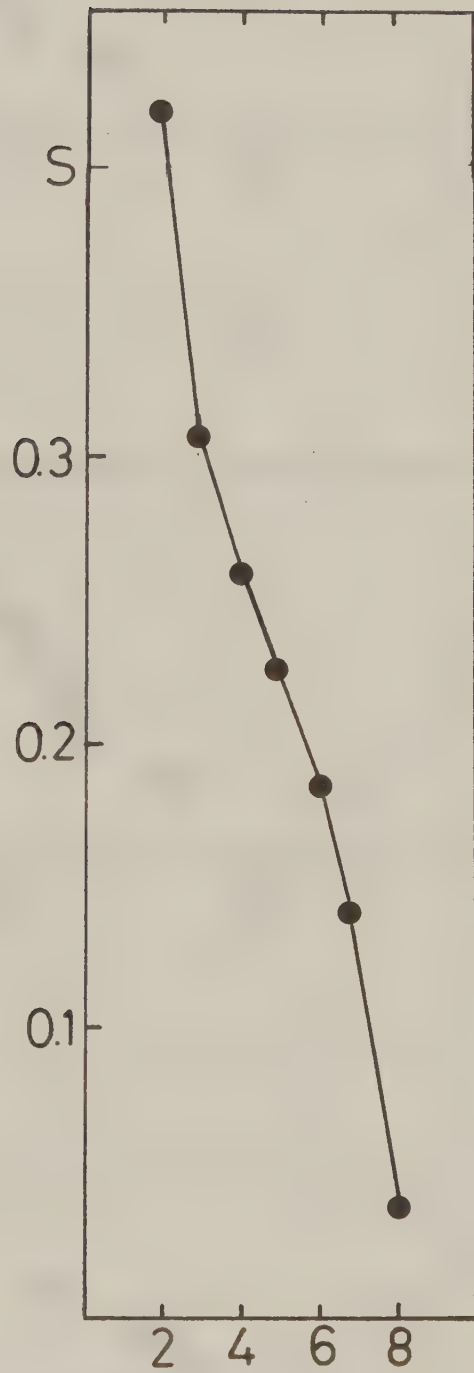
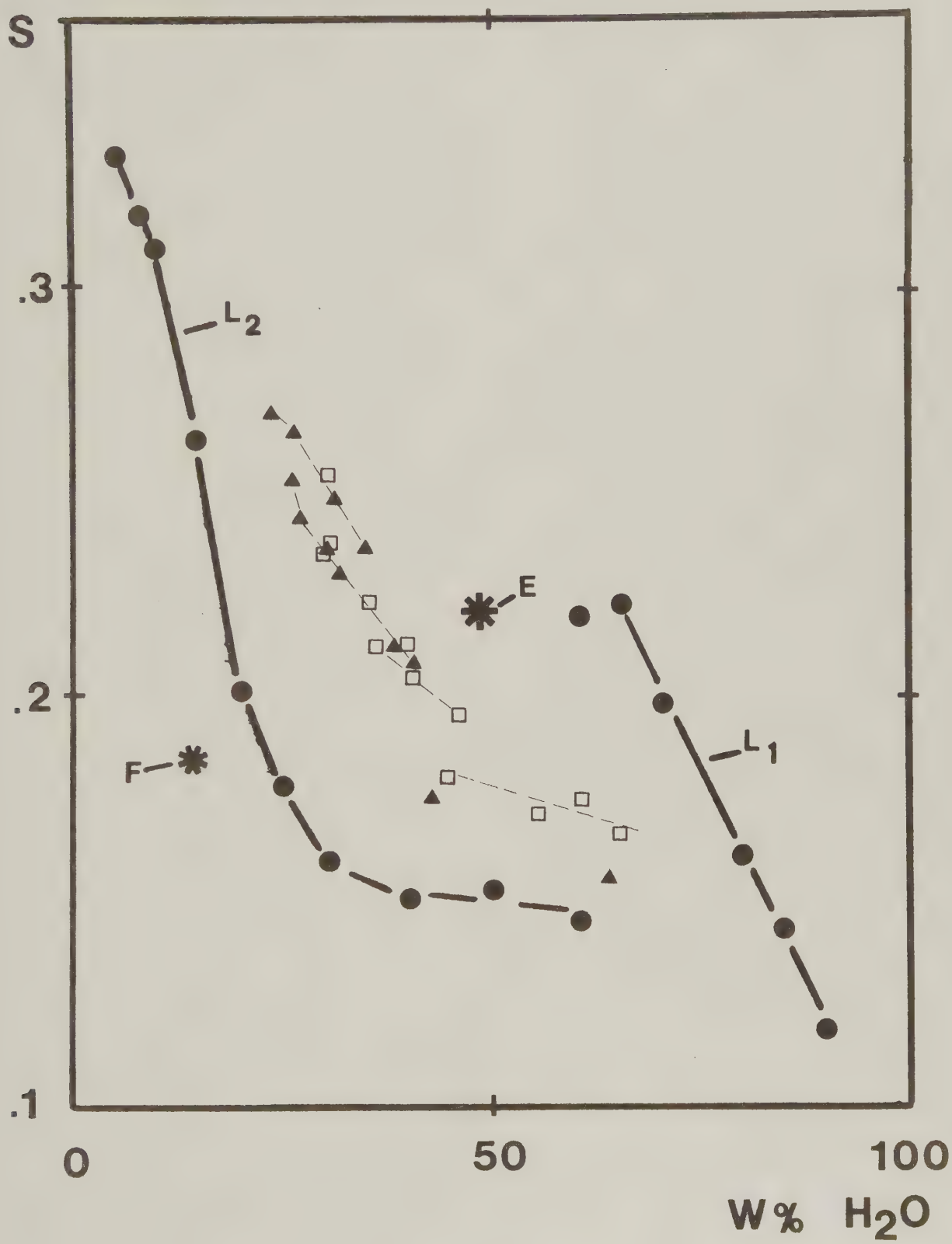


FIGURE 8



V

Fourier Transform Carbon-13 Relaxation and Self-diffusion Studies of Microemulsions

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Multi-field ^{13}C n.m.r. relaxation (spin-lattice relaxation and nuclear Overhauser enhancement) and multi-component Fourier-transform n.m.r. self-diffusion measurements have been applied to provide information on different aspects of the dynamic structure of microemulsions. Studies were performed over extensive concentration regions for four-component systems composed of sodium *p*-octylbenzene sulphonate, butan-1-ol, water and *n*-decane or toluene while limited investigations were made for other systems. The ^{13}C relaxation data were analysed on the basis of a two-step model of relaxation to provide information on short- and long-range molecular dynamics and on the degree of order of the alkyl chains with respect to hydrophobic-hydrophilic interfaces. The local motion of the alkyl chains is generally about as rapid (10^{-11} s) as that of liquid hydrocarbons. The effect of the organization in the system and the creation of hydrophobic-hydrophilic interfaces is a slight anisotropy in the molecular motion. This anisotropy is similar in magnitude to that of liquid-crystalline phases, but for the microemulsions the lifetime of the anisotropy is very short, one or two nanoseconds. According to the self-diffusion results, a closed water droplet structural model may apply for alcohols with longer alkyl chains. For the above-mentioned systems with butanol as cosurfactant the self-diffusion coefficients of both water and hydrocarbon are quite high and inconsistent with structurally segregated domains, unless these are very short-lived.

Much interest in the field of microemulsions is presently focused on structural and dynamic aspects, as these are important for both a fundamental understanding of the systems and the design of technical applications. While there is a range of systems which may be termed microemulsions, most work is concerned with four-component systems consisting of a surfactant, a medium-chain alcohol (butanol, pentanol or hexanol) as 'co-surfactant', hydrocarbon and water.¹⁻³ The structural problem can be expected to be more intriguing the shorter the alcohol. A change from, for example, decanol to butanol is expected to lead to dramatic structural changes in surfactant systems. Therefore, it was considered to be of particular relevance to study microemulsions with a cosurfactant like butanol. On the initiative of M. Kahlweit it was suggested, during the International Symposium on Surfactants in Solution (Lund, 1982), that coordinated studies were started between different groups on a particular model microemulsion system. This led to the formation of the 'European Microemulsion Group'. The system chosen for collaborative work within this 'Lund Project' was sodium *p*-octylbenzene sulphonate, butan-1-ol, water and decane or toluene. For a system of this type, where some of the components show

important pairwise miscibility, the relation to simple solutions is apparent. This miscibility is counteracted by the tendency of the surfactant to induce organized structures in aqueous systems. It seems, therefore, to be of particular interest to establish to what extent organized structures are formed as well as to characterize them dynamically, i.e. molecular conformation and order and structural lifetime.

In this paper we consider two methods which are applicable to these problems. First, magnetic field dependent ^{13}C n.m.r. relaxation of the different carbons provide information on the ordering of the chains with respect to internal interfaces, on chain dynamics and on slow motions extending over distances of the order of aggregate size. Order parameters are related to packing constraints given by interface curvature and are thus related to solution structure. Secondly, the translational motions over large distances of the different components provide information on aggregate geometry, the possible confinement to closed domains etc. There are a number of methods which are capable of providing self-diffusion coefficients but the Fourier-transform n.m.r. technique⁴⁻⁶ has several advantages: it is reliable and accurate and provides simultaneously the self-diffusion coefficients of all (normally⁴) components in a single rapid (normally 10 min or less) experiment without isotope labelling; difficulties arise if transverse spin relaxation is rapid but such problems are rarely prohibitive for ^1H and ^{13}C nuclei in microemulsions.

The present paper briefly describes the principles of the two approaches with reference to studies of simple surfactant systems. In particular, however, measurements are presented for the above-mentioned model system chosen for collaborative work. To cover in any detail a complex microemulsion system like this is a considerable undertaking; note that the ^{13}C relaxation study for any reliable analysis requires 4-6 sets of relaxation data (different fields etc.) for each of the 15-20 carbons for each sample composition. Our data are still far from complete, meaning that any full analysis is not yet possible. Further studies are underway to extend the data obtained from these microemulsion systems.

EXPERIMENTAL

SAMPLE PREPARATION AND CHEMICALS

The compositions of the different samples investigated in the self-diffusion studies are shown in fig. 1. The detailed phase diagrams of these two four-component systems are under study by P. Stenius' group in Stockholm and, of course, a correlation of the present findings with the phase equilibria will be an essential part of this research. The samples were prepared by weighing into glass ampoules (ca. 1 g total amount in a 3 cm³ ampoule for the diffusion work and ca. 10 g total amount for the relaxation work). After temporary sealing with rubber stoppers and cooling, the ampoules were flame-sealed, equilibrated at 25 °C and then inspected through crossed polarizers, if necessary, to determine the phase state. Isotropic solutions were then transferred to n.m.r. tubes for the measurements.

All samples were prepared from chemicals of puriss or equivalent grade chemicals. The sodium octylbenzene sulphonate was from the special batch prepared for the 'Lund Project' by P. Bothorel's group in Bordeaux to ensure sample uniformity between the various laboratories. Heavy water (Ciba-Geigy or Norsk Hydro, Rjukan, Norway, 99.8% ^2H enrichment) was needed to provide an internal field-frequency lock.

^{13}C N.M.R. RELAXATION AND ^{13}C - $\{^1\text{H}\}$ NUCLEAR OVERHAUSER EFFECT (n.O.e.) MEASUREMENTS

The ^{13}C T_1 relaxation measurements were performed at magnetic field strengths of 8.5, 2.1 and 1.4 T on a Nicolet NM 360 spectrometer, a Jeol FX-90Q spectrometer and a Jeol FX-60

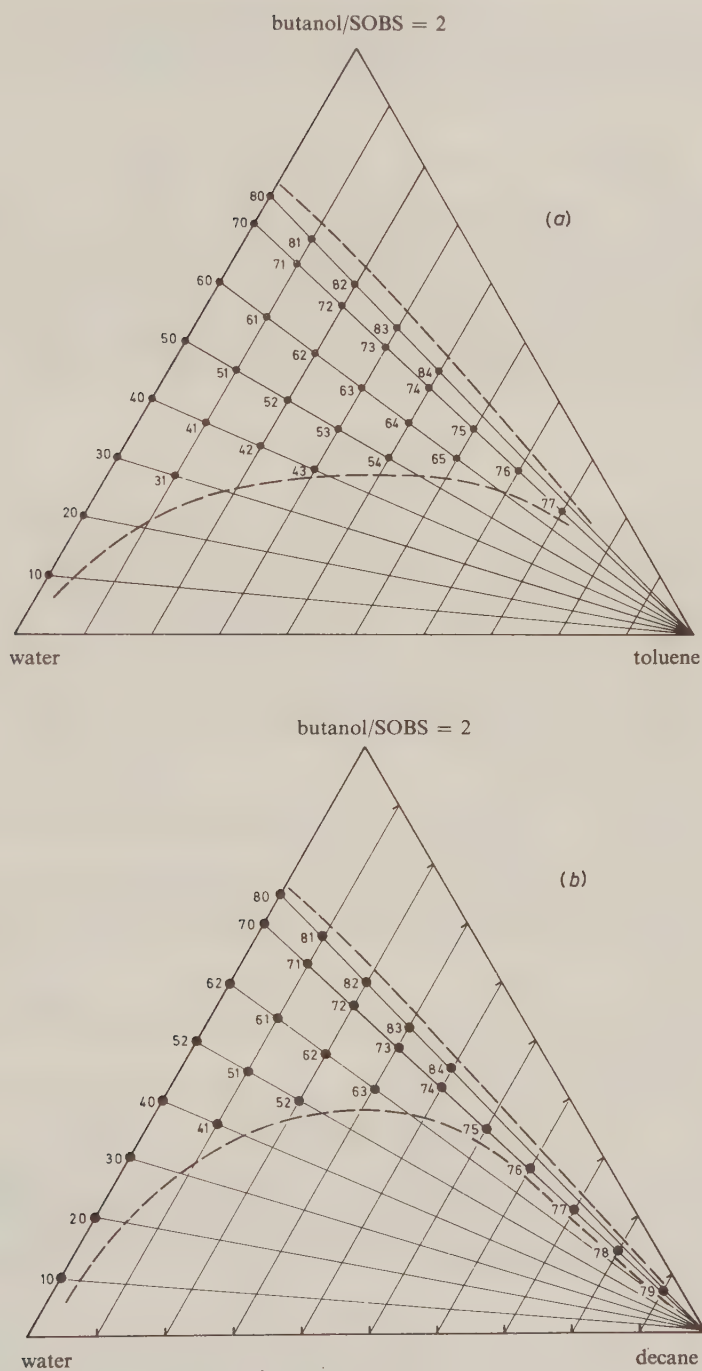


Fig. 1. (a) Sample composition notation and the result of a coarse trial and error phase-region investigation at 25 °C along the indicated dilution lines in the 'Lund project' system sodium octylbenzene sulphonate + D₂O + butan-1-ol + toluene (weight fractions). (b) The corresponding diagram for the analogous decane system at 25 °C.

spectrometer, respectively. The T_1 were measured using the fast inversion recovery technique. In addition, n.O.e. experiments were performed at 8.5 T on the Nicolet spectrometer. The detailed procedures for these measurements as well as for extracting the T_1 and the n.O.e. may be found elsewhere.^{7,8} The temperature was 27 °C for all relaxation measurements.

FOURIER-TRANSFORM N.M.R. SELF-DIFFUSION MEASUREMENTS

The measurement procedure has previously been outlined in a series of papers.⁴⁻⁶ The latest developments⁶ of these procedures make possible convenient and accurate multi-component self-diffusion studies through a single measurement series. Individual self-diffusion coefficients of each component (typically 4) in the concentrated microemulsion systems discussed in the present paper were measured on protons at 99.6 MHz and can be performed in < 10 min per sample. Water self-diffusion coefficients are evaluated from the averaged ROH-water proton signal according to a previously described procedure.⁹ All diffusion measurements were performed at 25 °C.

SELF-DIFFUSION

PRINCIPLES

The pulsed-gradient spin-echo experiment is a convenient method for the detection and measurement of the lateral displacement of matter. In the present implementation and application of the technique the self-diffusion in isotropic multi-component solutions is detected through a Fourier-transform procedure. It is important to note that individual molecular self-diffusion coefficients are measured separately and that the monitoring time is of the order of 100 ms. During this time span all measured (average) self-diffusion coefficients correspond to displacements over macroscopic distances several orders of magnitude larger than any structural element in the solution.

As discussed in earlier papers,⁹⁻¹³ knowledge of individual-component self-diffusion behaviour in multi-component solutions provides an unique source of information with regard to the solution structure.

In micellar solution the distinct separation of the hydrocarbon droplet-like micelles and the continuous aqueous pseudophase is reflected in very slow surfactant and solubilized hydrocarbon diffusion. Water diffusion is 1-2 orders of magnitude more rapid.¹⁴

Similarly, the distinct separation of water into droplets in a continuous hydrocarbon solution in inverted micellar solutions manifests itself in rapid hydrocarbon diffusion and very slow water diffusion.¹³

The term 'microemulsion' implies some rather distinct separation into hydrophilic and hydrophobic domains as well. According to our findings this is not normally the case.^{6,9-13} The prevalent structural model of 'microemulsions', up to very recently, has had an unfortunate origin in normal macroscopic emulsions. It has been argued that the simultaneous incorporation of large amounts of hydrocarbon and water into solution is accomplished through formation of emulsion-like aggregates, only of smaller size. Suggestions of bicontinuous structures of various kinds have also been made.¹⁵⁻¹⁹

Since isotropic solutions can be obtained over rather wide concentration ranges in 'cosurfactant microemulsion systems' also without surfactant, and since numerous examples of simultaneously water- and hydrocarbon-soluble compounds exist [e.g. alkylamides, substituted aromatics and short-chain alcohols (which exhibit quite large one-phase areas in three-component water + hydrocarbon systems)] it is more reasonable to use normal solutions as a starting point for any structural

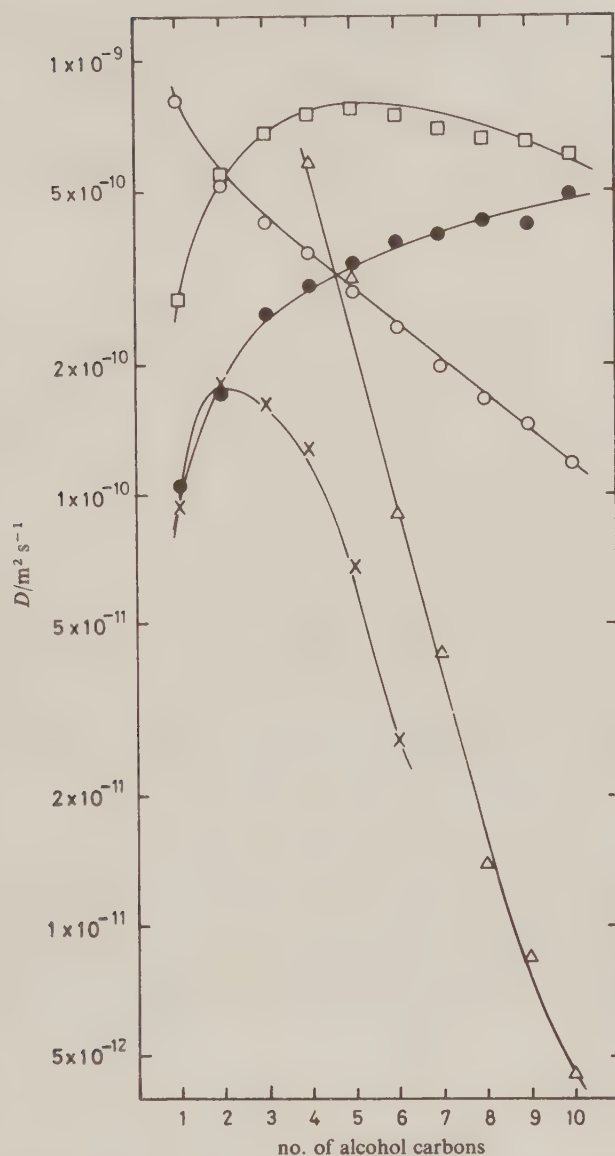


Fig. 2. Self-diffusion data at 25 °C in the toluene ($\square$) + D_2O ($\triangle$) + alcohol [$\circ$ and $\bullet$ (normalized)] + sodium dodecyl sulphate ($\times$) system (weight ratios 12.5:35.0:35.0:17.5, respectively). Water diffusion data for systems with short-chain alcohols were inaccessible under the present measurement conditions due to short transverse spin relaxation rates, as a result of intermediate proton exchange rates on the n.m.r. time-scale between water and hydroxyl protons.

tion patterns and the observation of well defined but small static (solid-type) effects in n.m.r. spectra.^{24,26-28} For micelles, a range of experimental techniques has demonstrated high intramolecular mobility; however, the micelles are still well defined distinct entities with long lifetimes.

On the basis of such a picture, Wennerström^{20,22,23} developed a two-step model

characterization of microemulsions. Only a few microemulsion systems exhibit self-diffusion behaviour consistent with the 'closed-droplet type', and our results indicate that different 'microemulsions' can structurally span the whole range between the two extremes. Their structure is sensitive to constituent as well as to the relative composition of the microemulsion. Only in one case, the AOT (sodium di-2-ethyl-hexyl sulphosuccinate) + water + hydrocarbon systems, have we found evidence for a distinct water-in-oil structural model within the whole, extensive isotropic solution region, regardless of the relative proportions of the constituents.^{9,13}

RESULTS AND DISCUSSION

Fig. 2 illustrates the very pronounced effect of the alcohol chain length on the component self-diffusion behaviour in a typical cosurfactant microemulsion.¹² It is seen that a maximum 'structure-breaking' effect occurs for C4–C5 alcohols, which parallels the behaviour of the composition extent of the isotropic phase region. Beginning with the C9 and C10 alcohols, the results do become consistent with a closed-water-droplet structural model, otherwise the degree of structural segregation between predominantly hydrophilic and hydrophobic constituents is evidently low. Note that although the alcohol self-diffusion coefficients decrease strongly with alcohol chain length, there is actually an increase in alcohol self-diffusion throughout the same series, when compared with the neat alcohols.

With reference to the sample compositions indicated in fig. 1 (a) and (b), the results of a systematic survey of the self-diffusion behaviour in the 'Lund project' systems is summarized in fig. 3(a)–(c). Except for the water-rich regions with essentially normal micelles, the diffusion coefficients are high and inconsistent with structurally segregated domains. For most surfactants rapid spin relaxation makes self-diffusion studies on the surfactant constituent impossible or difficult by our technique. The aromatic proton part of sodium octylbenzene sulphonate, however, has isolated bands with sufficiently long transverse relaxation times for a determination of the surfactant self-diffusion coefficients. As shown by the results in fig. 3(a)–(c), the surfactant diffusion is very rapid (typically 5 times more rapid than in micellar systems). This information clearly suggests that any local order and short-term aggregate size are less than those of micelles and that this particular isotropic solution phase cannot be much more organized than a partly associated liquid throughout most of its composition region. The most evident structural model would therefore be one of disrupted or distorted micelles for this and most other cosurfactant microemulsions.

¹³C RELAXATION

THEORY AND PRINCIPLES

A rather general important observation in n.m.r. relaxation studies of associated surfactant systems is that of rather long relaxation times combined with a marked magnetic-field dependence.^{20–23} This is incompatible with a single-exponential decay of the correlation functions describing the time dependence of the interaction of the nuclear spins. Instead it demonstrates that motions which span widely different time-scales make significant contributions to relaxation. An important feature of the current picture of surfactant systems such as micelles and liquid crystals is that of liquid character on the molecular level combined with marked organization and order over longer distances.^{24,25} As examples we cite the findings of diffuse high-angle X-ray diffraction in combination with characteristic low-angle X-ray diffrac-

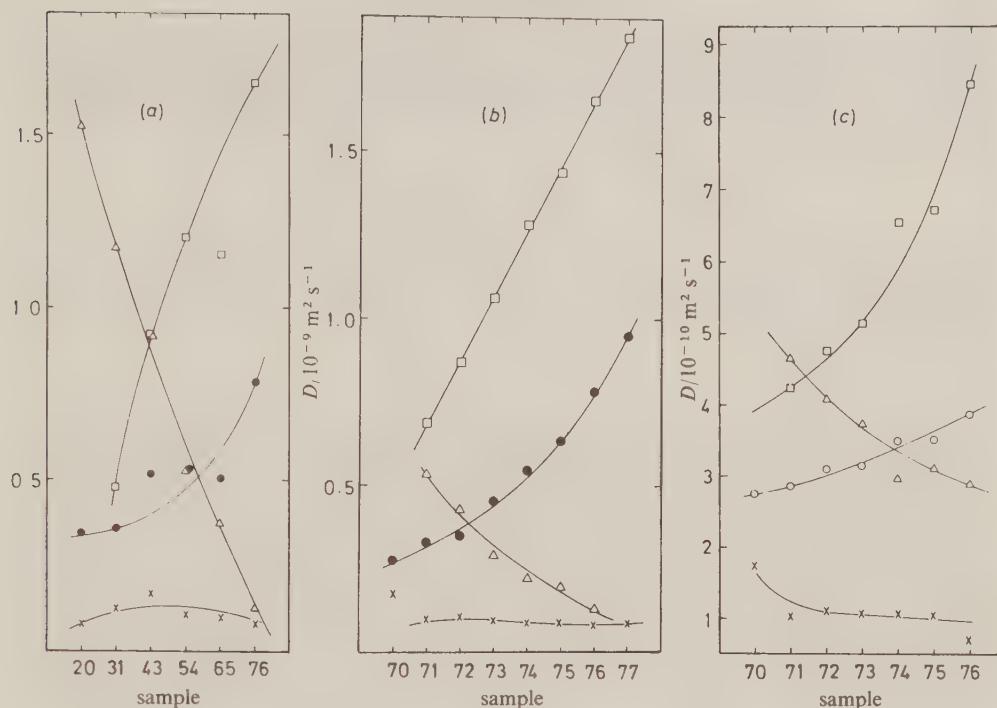


Fig. 3. Some self-diffusion results [with reference to the notation in fig. 1(a) and (b)] for the 'Lund project' systems. (a) and (b) Δ , water; $\square$, toluene; $\bullet$, butanol; $\times$, surfactant; (c) Δ , water; $\circ$, butanol; $\square$, decane; $\times$, surfactant.

of relaxation for microheterogeneous systems of the type considered here. The model assumes that the nuclear interaction is modulated in two steps over widely different time-scales. There are rapid local motions within the structure which do not give complete isotropy but reduce the interactions to a level which can be characterized by an order parameter. This is described, as for anisotropic liquid-crystalline systems, as the degree of orientation of a molecular vector with respect to the normal to a hydrophobic-hydrophilic interface. The remainder of the interaction must be modulated by motions which (isotropically) change the direction of the hydrophobic-hydrophilic interface. These motions fall in the range 10^{-7} – 10^{-9} s for solutions of spherical micelles or cubic liquid crystals. For rod micelles and anisotropic liquid crystals they are much longer. In fact, for the latter case they are generally too long (if the microcrystallites are not very small) to affect the n.m.r. parameters.

Detailed discussions on the interpretation of ^{13}C n.m.r. relaxation in microheterogeneous systems may be found elsewhere^{7,8,23} where investigations of two- and three-component surfactant systems are also reported. The expressions for T_1 and n.O.e. of ^{13}C are (under wide-band proton decoupling conditions) given by

$$\frac{1}{T_1} = \frac{N}{20} \left(\frac{\mu_0 \gamma_H \gamma_C \hbar}{4\pi r_{CH}^3} \right)^2 [\tilde{J}(\omega_H - \omega_C) + 3\tilde{J}(\omega_C) + 6\tilde{J}(\omega_H + \omega_C)] \quad (1)$$

and

$$\eta \equiv \text{n.O.e.} = \frac{1}{20} \gamma_H^3 \gamma_C \left(\frac{\mu_0 \hbar}{4\pi r_{CH}^3} \right)^2 N T_1 [6\tilde{J}(\omega_H + \omega_C) - \tilde{J}(\omega_H - \omega_C)] \quad (2)$$

where N is the number of protons directly bonded to the carbon atom, r_{CH} is the carbon-hydrogen distance (taken to be 1.09 Å) and the other symbols have their usual meaning. The various reduced spectral densities, $\tilde{J}(\omega)$, are for the applied two-step model of relaxation given by

$$\tilde{J}(\omega) = (1 - S^2)2\tau_c^f + S^2 \left(\frac{2\tau_c^s}{1 + (\omega\tau_c^s)^2} \right) \quad (3)$$

where τ_c^f and τ_c^s are the correlation times of the fast local and slow overall motions, respectively (exponential correlation functions are assumed), S is the (local) order parameter defined by

$$S \equiv \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle_f \quad (4)$$

where θ is the angle between the C—H bond vector and the local director, which is taken to be perpendicular to the hydrophobic-hydrophilic interface, and the symbol $\langle \rangle_f$ indicates an ensemble average over the fast local motion.

The two-step model of relaxation, as briefly sketched above, has been rather extensively applied for simple micellar systems.⁸ These studies have involved the determination of a larger number of experimental relaxation data than minimally required in the analysis, thus providing a critical examination of the model used. Significant support for the model is also provided by the close agreement between the deduced order parameters and those of liquid crystalline phases with similar composition.^{8, 29}

RESULTS AND DISCUSSION

¹³C relaxation studies were performed for 10 different sample compositions (see table 1) in different parts of the extensive isotropic-solution phase of the sodium octylbenzene sulphonate + butanol + toluene + water system. Measurements were performed of T_1 at 1.4 and 8.5 T and of the n.O.e. at 8.5 T while complementary measurements (mainly of T_1 at 2.1 T) were performed for some sample compositions and are under way for others. The experimental results are shown in fig. 4 and table 1. Note that in addition to a concentration dependence and a variation along the chain the main characteristics of the T_1 are that they are rather long at the same time as they are markedly field dependent; furthermore, the n.O.e. is below the theoretical upper limit (1.99). This demonstrates that there is an important contribution to relaxation from slow motions but also that these average only a small part of the total interaction [cf. eqn (1)–(3)]. As judged from the line width, T_2 is found to be rather long as well. Since T_2 are difficult to quantify for narrow lines they are not reported. However, the T_2 observations give support for the general interpretation. In particular, note that since T_2 is very strongly dependent on τ_c^s , the long T_2 show that τ_c^s cannot be very long.

Using the two-step model of relaxation as outlined above, the relaxation data (T_1 and n.O.e.) were analysed to provide the three parameters τ_c^f , τ_c^s and S . S and τ_c^f values along the chain are presented in fig. 5 and 6 for four sample compositions while τ_c^s data are presented in table 2.

While τ_c^f gives quantitative information on local alkyl chain dynamics, S and τ_c^s contain information on amplitude and time-scale of more long-range motions and are thus related to solution structure. The packing of surfactant alkyl chains varies with the shape of surfactant aggregate, sphere, reversed sphere, rod, lamellar etc.,^{30–33} and it has in particular been observed that the order parameter profile

varies with structure for liquid-crystalline phases.³⁴⁻³⁷ If aggregate rotation and molecular lateral diffusion are assumed to determine τ_c^s , then a small τ_c^s value implies high 'effective' curvature and is inconsistent with large ordered domains.

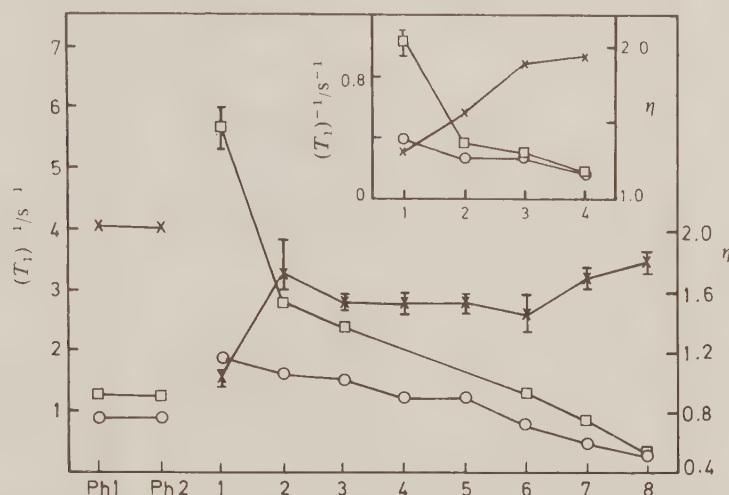


Fig. 4. Relaxation rate $(T_1)^{-1}$ and Overhauser enhancement (η) for sample 3 (see table 1 for sample composition) as a function of carbon position. The main figure refers to sodium octylbenzene sulphonate and the insert to butanol. $\square$ and $\circ$ refer to $(T_1)^{-1}$ measured at 1.4 and 8.5 T, respectively, while $\times$ refer to η measured at 8.5 T. The error bars correspond to an approximately 80% level of confidence. For points without error bars, the errors are smaller than the size of the symbols. Numbering of alkyl-chain carbons starts from the polar head-group. Ph1 and Ph2 refer to the *meta* and *para* carbons in the phenyl ring.

From the data in fig. 5 it is inferred that the order parameters are about as large in the microemulsions as in solutions of simple micelles and in liquid crystalline phases. This demonstrates a marked ordering of the alkyl chains over periods of the order of at least 10^{-9} s. For such periods there is no marked difference between the microemulsion solutions and liquid crystals (where, of course, ordering is on a long time-scale). However, if one considers τ_c^s a very clear difference is apparent. Thus it is striking that τ_c^s lies in the range 1–2 ns over a very wide composition range, demonstrating that the effective curvature of the hydrophobic–hydrophilic interfaces of the microemulsions seems to agree throughout with an effective radius corresponding to less than the length of the extended surfactant molecule. These findings are consistent with a predominance of small aggregates. If there are anisometric aggregates to an important extent, or if there are spheres (of oil or water) with radii markedly larger than the surfactant molecule length, then these findings indicate that the aggregates must be very flexible. In fact our results suggest that the hydrophobic–hydrophilic interfaces are very flexible and change direction extensively within a few nanoseconds. The rather even distribution of cosurfactant between different domains³⁸ reduces the interfacial energy and makes possible such high interface flexibility. The remark that with the considerable pairwise miscibility of components one should not be far from the rather structureless limit of simple solutions also points to such a situation.

As regards the τ_c^f values, they are of the order of 10 ps, which is close to what is observed for simple alkanes;^{8,39} an analogous observation has been made for lipid

Table 1. Observed T_1 relaxation times at two magnetic fields for carbons no. 1, 3 and 5 along the alkyl chain of sodium *p*-octylbenzene sulphonate

sample no.	T_1/s							
	C-1		C-3		C-5			
	8.45 T	1.4 T	8.45 T	1.4 T	8.45 T	1.4 T		
1 (0.08, 0, 0, 0.92) ^a	0.59 ± 0.01	0.31 ± 0.02	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>		
2 (0.10, 0, 0, 0.90)	0.56 ± 0.01	0.34 ± 0.02	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>		
3 (0.076, 0.05, 0, 0.874)	0.56 ± 0.02	0.17 ± 0.02	0.62 ± 0.05	0.42 ± 0.02	0.87 ± 0.05	0.87 ± 0.05		
4 (0.095, 0.05, 0, 0.855)	0.53 ± 0.02	0.20 ± 0.03	0.77 ± 0.02	0.44 ± 0.04	0.94 ± 0.02	0.94 ± 0.02		
5 (0.068, 0.15, 0, 0.782)	0.60 ± 0.05	0.30 ± 0.03	0.75 ± 0.05	0.60 ± 0.05	1.27 ± 0.05	1.27 ± 0.05		
6 (0.085, 0.151, 0, 0.764)	0.56 ± 0.01	0.28 ± 0.03	0.87 ± 0.05	0.50 ± 0.03	1.16 ± 0.03	1.16 ± 0.03		
7 (0.080, 0.720, 0, 0.20)	0.48 ± 0.04	0.39 ± 0.06	0.95 ± 0.05	0.67 ± 0.04	1.30 ± 0.09	1.30 ± 0.09		
9 (0.144, 0.255, 0.45, 0.152)	0.57 ± 0.05	0.30 ± 0.03	0.97 ± 0.03	0.72 ± 0.02	1.64 ± 0.04	1.64 ± 0.04		
10 (0.20, 0.35, 0.20, 0.25)	0.56 ± 0.04	0.27 ± 0.01	0.92 ± 0.02	0.65 ± 0.02	1.50 ± 0.07	1.50 ± 0.07		
11 (0.14, 0.257, 0.140, 0.46)	0.60 ± 0.02	0.29 ± 0.03	0.86 ± 0.05	0.62 ± 0.02	1.41 ± 0.05	1.41 ± 0.05		

^a Weight fractions in order: surfactant, butanol, toluene, water. ^b No measurements made because of insufficient resolution.

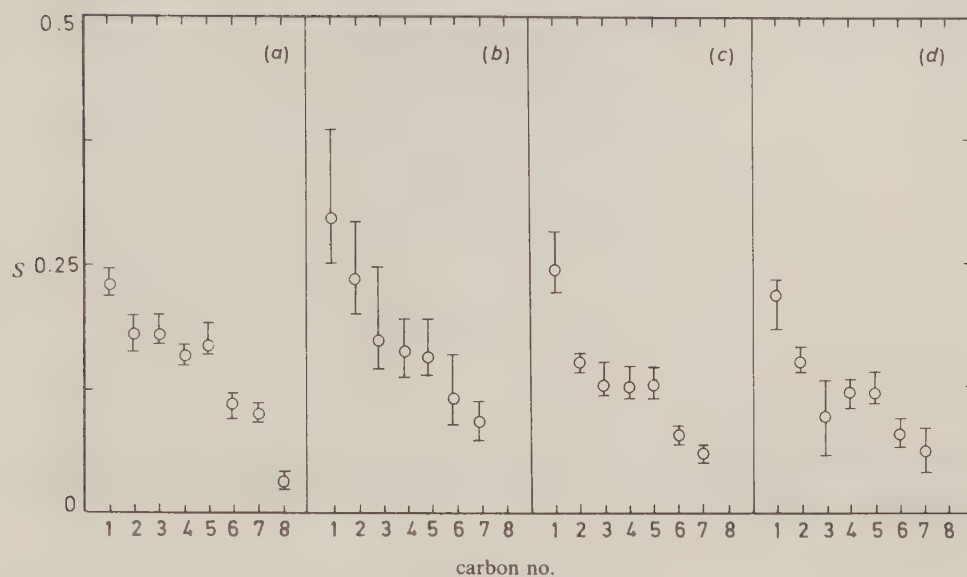


Fig. 5. The order parameter (see under Theory and Principles) for the alkyl chain of sodium octylbenzene sulphonate in four samples. (a), (b), (c) and (d) correspond to samples 1, 5, 9 and 11, respectively (see table 1 for sample compositions). Numbering of carbons starts at the carbon closest to the phenyl ring. The error bars correspond to an approximately 80% level of confidence.

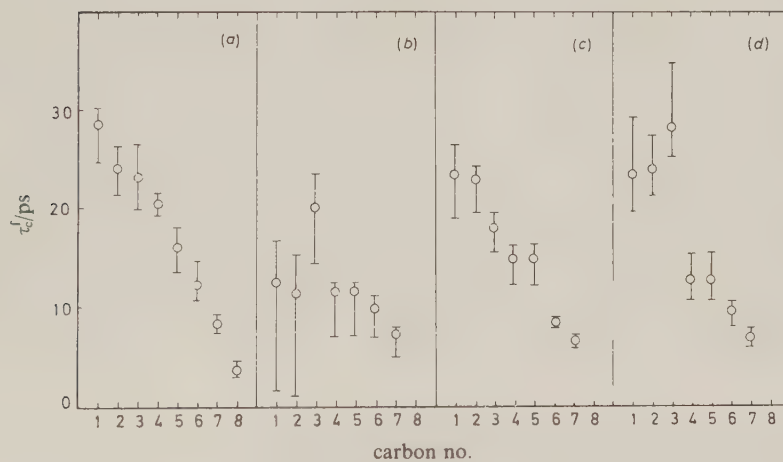


Fig. 6. The fast correlation time (see under Theory and Principles) for the alkyl chain of sodium octylbenzene sulphonate in four samples. (a), (b), (c) and (d) correspond to samples 1, 5, 9 and 11, respectively (see table 1 for sample compositions). Numbering of carbons starts at the carbon closest to the phenyl ring. The error bars correspond to an approximately 80% level of confidence.

Table 2. Slow-motion correlation time, τ_c^s , for different sample compositions (given in table 1)

sample	$\tau_c^s/10^{-9}$ s
3	1.8 ± 0.4
4	1.3 ± 0.4
5	0.8 ± 0.2
6	1.7 ± 0.5
7	1.0 ± 0.8
9	1.1 ± 0.3
10	1.7 ± 0.4
11	1.7 ± 0.5

bilayers in liquid crystals.⁴⁰ τ_c^f decreases on moving away from the polar head. For alkanes and non-polar derivatives thereof, the correlation time varies little between different methylenes.

CONCLUSIONS

There is at present no theoretical model available against which we can quantitatively test our results. Whilst awaiting the development of such models one may loosely talk about the degree of structure or organization in the isotropic solution phases. In one limit one has the structureless case of simple solutions such as alcohol + water mixtures and in the other (for surfactant systems with liquid chains) the well organized liquid crystals. The microemulsions clearly fall in between these two situations.

Both the present approaches, i.e. Fourier-transform n.m.r. self-diffusion and multifield ¹³C n.m.r. relaxation, are sensitive to the degree of structure in the system but in very different ways. The self-diffusion results emphasize that over wide concentration ranges there are no marked long-lived structural barriers to translation over macroscopic distances for either hydrophilic or hydrophobic compounds. The self-diffusion work also emphasizes that this situation is extremely dependent on cosurfactant chain length. The ¹³C relaxation results show that the motion of the alkyl chains is about as rapid as that of liquid hydrocarbons and emphasize also that a substantial fraction of the surfactant molecules are oriented and have marked motional anisotropy. Thus there is organization in the system and the creation of hydrophobic-hydrophilic interfaces which induces slight anisotropy in the motion. This anisotropy is similar in magnitude for the microemulsions as for liquid crystalline phases and micelles but for the microemulsions the lifetime of the anisotropy is very short, one or two nanoseconds.

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VI

NONIONIC SURFACTANTS IN NEAT LIQUID AND MICELLAR SOLUTION
STUDIED BY C-13 NMR RELAXATION AND CHEMICAL SHIFTS

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ABSTRACT

The C13-NMR chemical shifts and spin-lattice relaxation times have been determined for nonionic oligo oxyethylene dodecyl ether surfactants (C12Ex) in water (C12E5) and as neat liquids (C12E3, C12E4, C12E5 and C12E6). For the ethylene oxide chains the chemical shifts suggest that the trans conformers become more stable as the temperature is increased or if the environment is made more apolar. This agrees with the predictions of a recent theoretical model for ethylene oxide chains. The ordinary upfield shift corresponding to increased population of gauche conformers was observed for the alkyl chains at increased temperature.

The spin-lattice relaxation for micellar and neat nonionic surfactants was found to be magnetic field dependent. Using the so-called two-step relaxation model of Wennerstrom we have obtained order parameter and fast correlation time profiles in addition to a slow correlation time. These parameters provide novel information on the nonionic surfactant aggregates in water and on the structure of neat nonionic surfactant liquids.

C13-NMR spectra of C12E5 in anisotropic phases show unusually narrow lines an observation providing information on chain order.

I N T R O D U C T I O N

The aggregation behaviour in aqueous systems of nonionic oligo(ethylene oxide) surfactants are currently intensively studied: micellization(1), micelle size and shape(2-5), phase behaviour(6), microemulsions(7,8), liquid crystalline phases(9-11), etc. The nonionic surfactants differ in many respects from ionic surfactants: more self-association cooperativity, micellar shape, clouding phenomenon, phase inversion in three-component systems with hydrocarbon, stability of liquid crystalline phases and so on.

It should be possible to rationalize many of these features from simple considerations if basic molecular aspects were understood. The only difference between ionic surfactants and nonionic surfactants is the head group and therefore it is important to understand the (temperature dependent) hydration of the oligo(ethylene oxide) chains and the conformational behaviour of these as well as of the alkyl chains.

While, the hydration of these micelles was recently determined from self-diffusion measurements(12), there seems to be no direct information on the chain conformations in the isotropic solutions or in the liquid crystals.

In these systems, NMR relaxation in principle gives direct information on chain motions and ordering(13,14). ^1H and ^2H relaxation demand specific labelling because of a narrow chemical shift range and other complications.

Therefore, ^{13}C NMR is often the only realistic alternative. The much broader shift range ensures a reasonable number of assignable signals. The sensitivity, however, will be a problem at lower concentrations.

A general problem in NMR relaxation studies of organized systems like micelles and microemulsions is that the simple relations applicable to simple liquids and solutions do not apply. The reason is that there are motions on widely different time scales which induce relaxation and these motions modulate different parts of the interaction; the rapid motions are in the extreme narrowing range while the slow ones are in the nonextreme narrowing range. In several systems one observes ^{13}C spin-lattice relaxation times (T_1) that would, in the frame of the simple relaxation model, give correlation times well in the extreme narrowing range. However, this is in contradiction with the observed frequency dependent relaxation(13,15).

A theory of NMR relaxation in surfactant systems has been presented by Wennerstrom et al.(13) and has been tested rather extensively for ionic surfactant micelles(14-17), and microemulsions(15,18,19). For spherical ionic micelles motions on two different time scales are shown to be sufficient to explain the relaxation data. Thus, there are fast anisotropic local motions (like gauche-trans isomerism) in the 10-30 ps range that average most of the interaction and then there are slow overall motions (like micelle reorientation) which are isotropic. For microemulsions a more complicated motional situation may occur and a third

intermediate anisotropic motion is present(19).

This article reports measurements of C^{13} -NMR relaxation at three different magnetic field strengths:(1.40T, 2.34T and 8.45T) of alkyl oligo (ethylene oxide) surfactants which aim at characterizing the state of the alkyl and the ethylene oxide chains. We report data of neat C12E3, C12E4, C12E5 and C12E6 liquids at 27C and of normal micellar solutions of C12E5 at 27 and 6C. Furthermore, C^{13} chemical shift data are reported as a function of concentration and temperature. The chemical shift data indicate differences between the alkyl and ethylene oxide chain carbons with respect to temperature and concentration variations. The alkyl carbons follow the ordinary pattern as for ionic micelles but the ethylene oxide carbons have an opposite behaviour.

EXPERIMENTAL SECTION

All samples were prepared by weighing into NMR tubes which then were provided with vortex plugs, closed with caps and secured with tape.

The oligo(oxyethylene)dodecyl ether surfactants C12E3, C12E4, C12E5 and C12E6 were of highest quality and obtained from Nikko Chemical Co. Ltd., Tokyo. The heavy water was obtained from Ciba-Geigy and the isotopic purity was better than 99.7 at.%.

The relaxation measurements were done at three magnetic field strengths; 1.4 T, with a Jeol FX-60, 2.34 T, with a Varian XL-100 or Jeol FX-100, and 8.5 T with a Nicolet NIC-360 spectrometer. Typical parameters in the experiments were: 10 to 12 pulse interval times from .05s to 6.0s. The time between the pulse sequences was at least 6s. The relaxation times were calculated through a three parameter fit. The estimated error in the relaxation times was 10% at the two lowest fields and 5% at the highest field. The uncertainty in temperature was $\pm 1^{\circ}\text{C}$. For further details of the relaxation experiment, see reference 15.

The chemical shifts were measured at the highest field strength, 8.5 T, with the Nicolet spectrometer. The nonionic surfactant spectra were assigned according to Ribeiro and Dennis(20).

The chemical shift reference was the lock signal (D2O) or the terminal methyl group. For details see the text.

RESULTS

C^{13} - CHEMICAL SHIFTS

Micellar phase

The chemical shifts are nearly constant at 27°C and 6°C as the surfactant concentration is increased (table 1). This indicates there are no changes in the conformational state of the surfactant molecules. All measured concentrations are well above the critical micelle concentration.

Table 1. C13-NMR chemical shifts (ppm) of C12E5 as a function

of concentration at two different temperatures, 27C and 6C. C1 is the terminal methyl carbon and it is taken as an internal reference.

at 27 C

C12E5 W%	2.34	9.90	14.98	25.31	34.20
C21	58.15	58.15	58.16	58.16	58.17
C12	57.21	57.19	57.21	57.20	57.20
C13	56.25	56.24	56.24	56.25	56.26
C15-18	56.09	56.08	56.10	56.10	56.11
C19	56.00	55.99	56.00	56.01	56.02
C20	55.82	55.81	55.83	55.83	55.84
C22	46.64	46.64	46.65	46.65	46.65
C3	18.17	18.16	18.17	18.17	18.16
C7-10	16.11	16.10	16.12	16.11	16.10
C7-10		16.02	16.03		16.03
C7-10		15.94	15.95	15.95	15.94
C4,6	15.78	15.76	15.78	15.78	15.78
C4,6	15.69	15.67	15.69	15.68	15.67
C11	12.36	12.35	12.37	12.36	12.36
C2	8.81	8.80	8.82	8.81	8.81
C1	0	0	0	0	0

at 6 C

C12E5 W%	2.39	9.90	14.98	25.31	34.2
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C21	57.99	57.99	57.99	58.00	57.99
C12	57.13	57.12	57.13	57.14	
C13	56.04				
C15-18	55.93	55.92	55.92	55.94	55.92
C19	55.85				
C20	55.64	55.65	55.65	55.66	55.65
C22	46.43	46.44	46.43	46.45	46.43
C3	18.21	18.20	18.21	18.21	18.21
C7-10	16.21	16.21	16.21	16.20	16.22
C4,6	15.71	15.78		15.77	15.79
C4,6	15.67	15.68	15.69		
C11	12.33	12.33	12.33	12.34	12.34
C2	8.84	8.84	8.84	8.84	8.85
C1	0	0	0	0	0

From the table above, also the assignment of the signals can be noticed.

Neat compared with micellar surfactant

In fig. 1, the shift difference between neat and micellized C12E5 is displayed. We find a up field shift for the ethylene oxide part and a low field shift for the alkyl chain part of the neat when compared to micellized C12E5.

Temperature dependence in the micellar phase

We have plotted the chemical shift difference between micellar C12E5 at two temperatures 10C and 45C (see fig. 1). A low field shift is found for the alkyl chain and a up-field shift for the ethylene oxide part. No shift changes are seen at the C12-carbon.

A more detailed temperature dependence of the chemical shifts between 10C and 45C is shown (fig. 2) for some carbons in the chain. The strongest temperature dependence carbons show in the ethylene oxide part. The terminal methyl shift is about .3 ppm. If the temperature dependence of the lock signal is taken into account (0.38 ppm) (21) the terminal methyl group is shifted only .08 ppm down field.

C13-RELAXATION

Concentration and temperature dependences

In fig. 3. we see the relaxation rates of some alkyl chain methylenes and some ethoxide chain methylenes as a function of surfactant concentration at two different temperatures. All samples investigated are above the critical micelle concentration (CMC). We observe only slight changes in the relaxation rates when the concentration is changed. This is what we commonly find for spin-lattice relaxation in L1-phases in ionic(22) and nonionic(23) systems well above the CMC.

Magnetic field dependence of micellar surfactant relaxation

There is a substantial field dependence in the relaxation rates at both 27C and 6C (see figures 4 and 5).

The field dependence is largest in the middle of the chain and small at both ends of the molecule. The field dependence is larger at low temperature.

Magnetic field dependence of neat surfactant relaxation

In figure 6, relaxation rate profiles for neat nonionic surfactants, C12E3, C12E4, C12E5 and C12E6 are displayed.

It is a striking feature that the relaxation rates of the terminal ethylene oxide and methyl groups are independent of the molecular size. The main differences in the relaxation rates are located to the middle of the chain.

In fig. 7. field dependent relaxation rates of neat C12E4 and C12E5 are displayed. We have additional measurements of C12E3 and C12E6 that also show a considerable field dependence. A considerable anisotropy in the fast local motions can be inferred. The anisotropy increases when approaching the hydrocarbon / ethylene oxide chain connection.

SPECTRA OF ANISOTROPIC PHASES

An interesting observation is that lamellar and hexagonal phase samples of C12E5 in water give C13 NMR spectra with quite narrow lines (see fig.8.) which is contrary to what is found for ionic surfactants.

We expect this to be a general behaviour of nonionic surfactants since this has also been observed in the C12E6-water system(24). This phenomenon gives many further possibilities to get novel information on the anisotropic phases through C13 relaxation (the Wennerstrom model should apply) and chemical shift studies. For ionic surfactants this is also possible to do if the sample is aligned at the magic angle(25), but the technique is not so easy to apply.

DISCUSSION

C13-CHEMICAL SHIFTS

Concentration and temperature dependence

Surfactant self-diffusion and proton NMR line widths(3) are interpreted to show an increase in aggregate size when the temperature or concentration is increased in the micellar L1 phase of C12E5 and water. The micellar aggregation number can be several hundreds. The C12E5 micelle at low temperatures tend to become rodlike when approaching the hexagonal phase(6,26) (see fig. 9.) but at higher temperatures when approaching the lamellar phase, the situation is less clear, but even here rodlike micelles might exist(27).

In a recent theory of oligo ethylene oxide-water phase behaviour(28,29), the miscibility gap is interpreted as caused by the different nature in the high- and low-temperature states of the ethoxide chain. Two conformations of 27 possible were taken as low-temperature state for the ethylene oxide segment. The rest, excluding two sterically hindered conformations, was taken as the high-temperature state. The low temperature state consists of the two gauche conformations around the C - C bond and trans for the C - O bond. These states are shown by theory and experiments (see ref.29 and references therein), to be more stable in a polar environment than the other conformations.

C13 chemical shifts in alkyl chains have been shown to depend on the gauche/ trans ratio(30) and less on the environment(see ref.31 and references therein). In the ethylene oxide segment we have the same gauche/trans isomerism for the carbon-carbon bond but then we also have the two carbon-oxygen bonds that will complicate the situation. It is likely that medium effects (like hydrogen bonding to the oxygens) will influence the shifts of the ethylene carbons. However, as seen later in the discussion, hydrogen bonding would give opposite shifts to what is observed. This indicates that the possible medium effects on the shifts will be over ruled by the gauche/trans shift (estimated to 4.8ppm).

Summarizing, we expect the C13 chemical shifts of the ethylene oxide chain to be sensitive to the gauche/trans ratio of the C-C bonds(as in alkyl chains) and according to the theory above, also the polarity of the environment, since altered polarity induces changes in the gauche/trans equilibrium.

To test this prediction the chemical shifts of C12E5 as monomers, in micelles and as neat liquid can be measured. Also the temperature can be varied for a micellar solution to change the polarity of ethylene oxide environment (water).

In general down-field C13 chemical shifts are observed for the alkyl chain carbons when surfactant monomers are aggregated into micelles(31-33). This is interpreted as a

consequence of an increased amount of trans conformations in the chain. The maximum in the shift difference is located at the middle of the chain.

In figure 1, we display the shift difference between micellized and neat C12E5. The shift scale is without any corrections. However, there is a slight difference between the lock-signals in the two samples. The neat C12E5 sample is locked on heavy water placed coaxially in a outer 12 mm NMR tube. The micellized C12E5 is locked on internal heavy water. It has been shown that the water proton shift is shifted upon addition of for example sodium dodecyl sulfate(34) and that the terminal methyl protons are quite invariable. As seen from figure 1, the terminal methyl is not shifted much at the uncorrected scale. If we choose the terminal methyl group as an internal reference the zero-level is shifted as indicated by the lower dashed line.

We observe a down-field shift for the alkyl chain carbon when going from neat to micellized C12E5. This is interpreted as an increased trans state for the chain. The micelle structure would thus more restrict the available conformations for the alkyl chain compared to the structure in the neat surfactant state. For the ethylene oxide chain part, we observe an up-field shift for the micellized C12E5. At first sight this seems to be peculiar. Regarding the water-ethylene oxide chain interaction, the hydrogen bonds would deshield water protons and the ethylene oxide and thus cause a down-field shift. In the neat surfactant liquid, only the terminal OH-groups could form hydrogen bonds.

However, according to the theory for ethylene oxide chain conformations, the gauche state is more stable in more polar environment. This would then explain the experimental up-field shift for micellar C12E5 ethylene oxide part despite the presumed down-field shift due to increased hydrogen bonding.

Corno et al. (32) investigated C13 chemical shifts of C12Ex ($x=2,3...10$) upon micellization in water. They concluded that both in the alkyl and ethylene oxide parts an increase in the amount of trans states resulted. Thus, the alkyl part follows the behaviour of ionic surfactants and the ethylene oxide part behaviour is in accordance with the generally predicted increased trans state stability in more apolar environment.

As it is experimentally observed and theoretically predicted the gauche/trans isomerism equilibrium in the ethylene oxide chain is changed if the polarity of the environment is changed. Therefore, the chemical shifts would then indirectly reveal changes in the hydration. As seen from table 1., there is no concentration dependence in the chemical shifts of the ethylene oxide carbons. Thus, we conclude that above the CMC there is no change in the hydration. Also other observations support this conclusion. Nilsson et al. (26) found from water diffusion measurements that hydration is independent of ethylene oxide chain length and that 4-6 water molecules per ethylene oxide segment were perturbed. A slight concentration dependence (decrease) was observed. However, in view of an improved theory of water

self-diffusion in colloid systems(35) the hydration is expected to be concentration independent as long as full hydration can be maintained. Water ^{17}O relaxation studies(36) indicate that the interaction between water and ethylene oxide segments is independent of ethylene oxide chain length but temperature dependent and that the activation energy is different from that of pure water.

Temperature dependence

If we compare chemical shifts for the alkyl chain part at two different temperatures we observe low-field shifts with decreasing temperature (fig.1). This indicates an increased amount of trans states in the chain. Larger effects are present when neat and micellized C12E5 are compared. The ethylene oxide carbons are shifted to low field (increased trans state) and the alkyl chain carbons are shifted to high field (increased gauche state). At the hydrocarbon chain ethylene oxide chain interface small shifts changes are seen.

We have also studied the ^{13}C -NMR chemical shifts for micellized C12E5 as a function of temperature. In figure 2, some results are shown. The shifts are relative those of 10°C and the sample is locked at internal heavy water. The water lock-signal is shifted up-field when the temperature is increased. This is due to the decreased hydrogen bonding and the shift is relatively linear(21).

We have chosen to measure our chemical shifts relative the lock signal (D2O) since the temperature dependence of the standard reference TMS seems to be debated(37,38).

If we make the correction for the temperature dependence of the lock signal the terminal methyl group will be shifted less than 0.1 ppm up-field.

C13-RELAXATION

As is evident from figure 4, there is a field-dependence in the relaxation. From these data we are able to calculate the order parameters and the fast and slow motion correlation times using the so called two-step relaxation model(13). In equation (1) the relaxation rate is given as a function of these parameters and the frequency. where $k = \frac{\text{constant}}{\tau_c^f}$, S is the order parameter, τ_c^f is the fast correlation time, τ_c^s is the slow correlation time and ω_c and ω_H are resonance frequencies of the C13 and H1 nuclei.

$$\frac{1}{T_1} = \left[\frac{\mu_0 \hbar \gamma_C \gamma_H}{4\pi r_{C-H}^3} \right]^2 \left\{ 2(1-S^2)\tau_c^f + S^2 \frac{1}{5} \left\{ \frac{3\tau_c^s}{1 + \omega_c^2 \tau_c^s{}^2} + \frac{\tau_c^s}{1 + (\omega_H - \omega_C)^2 \tau_c^s{}^2} + \frac{6\tau_c^s}{1 + (\omega_H + \omega_C)^2 \tau_c^s{}^2} \right\} \right\} \quad (1)$$

Order parameters

Using the two-step model we determined the order parameter profiles for micellar C12E5 at two temperatures(fig.10,11). Since there was no concentration dependence in the relaxation rates, there will not be any concentration dependence in the order parameters or fast correlation times. Slightly higher order is found at low temperature, but the profile is not changed.

If the aggregates are rodlike the relaxation expressions will be modified. Then the order parameter values increase by the square-root of $4/3$. The relatively narrow $C13$ -NMR lines in the micellar and lamellar phases would then suggest a considerable flexibility of the aggregates.

The presence of an anisotropy averaged by a slow motion suggests that the neat nonionic surfactants are strongly aggregated. Pure hydrocarbon and poly ethylene oxide are phase separated at this temperature. Accordingly, the hydrocarbon part and the ethylene oxide part of the nonionic surfactant avoid each other by occupying different domains and some kind of a structure is formed.

In figure 12. the order parameter profile is shown for $C12E4$ and $C12E5$. The order parameters are the same within experimental error between $C12E4$ and $C12E5$.

Fast motion correlation times

In figure 13. the deduced fast motion correlation times along the alkyl and ethylene oxide chains are shown. We observe that the maximum motional restriction is not at the alkyl/ethoxid chain connection but shifted more to the ethoxid chain part. Low field measurements(39-41), have previously been interpreted to show a maximum in the motional restriction at the alkyl/ethylene oxide connection. The reason for this discrepancy can be explained by the results for the order parameters in figure 13.

The highest order is found at carbon number 11 and the order is reduced when going to either the terminal methyl or the terminal ethylene oxide. According to equation (1) we obtain the largest contribution to the relaxation from the slow part for the highest order parameter. At lower fields this contribution is particularly large. The measured relaxation rates are influenced by the order parameter, the slow motion and the field strength. Thus, the fast motion cannot be determined from single low field measurements.

Heatley et al. (23) recently published a proton NMR relaxation study where they found frequency dependent relaxation for, among others, C12E27 methyl ether. The H1 relaxation process is complicated by the presence of both intra- and inter-molecular contributions but still some interesting observations could be made. Thus, they found the highest order close to or at the alkyl/ethylene oxide conjunction depending on the nonionic surfactant. In the ethylene oxide part very low order was found. Concentration dependence of T1 and T2 was very weak for C14E27CH3. Many of these observations parallel our findings from C13 NMR relaxation in the C12E5 system.

For ionic surfactants no dramatic changes as the concentration is varied are seen for the fast local motions in the micellar solution (14,22). At the highest field we have a quite small contribution to the relaxation from the slow motion and essentially we then see only the fast local motions. The fast local motion profile clearly shows that the molecule is not behaving as free molecule (the mobility

minimum would then be located at the center of the mass). Since the micelles are thought to be large a further increase of the size is not likely to significantly change the molecular environment. Also at these concentrations there is enough water to fully hydrate the ethylene oxide chains. We therefore expect concentration independent relaxation in the L1-phase.

Also the fast motion correlation times are very similar as seen in figure 15. This indicates that the order and motional freedom is not very sensitive to ethylene oxide chain length.

Slow motion

A multi-parameter fit (in principle we have three unknown parameters per carbon but one of them, the slow correlation time should be common and therefore the number of free parameters will substantially be reduced) to these data resulted in error sums (defined as the sum over all squares of differences between the observed and calculated values divided by the square of the observed value) below 0.13. The slow correlation was fixed during the fitting. Different values between 1 and 8 ns were then chosen to investigate the error sum. The error sum increases with increasing slow correlation time according to table 2.

Table 2. Sum of error as a function of the slow correlation time for the different C12Ex relaxation data.

Compound	slow correlation (ns)	sum of errors
C12E4	1	0.122
	2	0.160
	5	0.184
	8	0.224
C12E5	.8	0.048
	1	0.054
	2	0.077
	5	0.093
	8	0.123

The error sum indicates that the fit is within the experimental error. We have chosen the slow correlation to be 1 ns. The reason to this is that the minimum in the iteration is very shallow and thus the slow correlation time is badly determined. Below 1 ns the error sum still decrease but some parameters will get unphysical(negative) values. For determining the slow correlation time lower field measurements should be done for instance with deuterated compounds. This would also reveal other possible slow correlation times.

At low temperature, there was a better characterized minimum in the iteration and therefore, we also got narrower error limits for all parameters.

Neat compared to micellized C12E5

Since the CMCs of these nonionic surfactants are very low ($< 10^{-5}$ M), we are not able to compare the monomeric state with the micellized one. However, we are able to compare the micellized state with the state of neat surfactant. Comparing figs. 13 and 15 we note that the fast correlation times of these two states are the same within experimental error besides for the terminal ethylene oxide unit. In the micellar state the mobility is higher and this might be due to the different environment. For the order parameters some higher values are obtained for the neat surfactant but the order parameter profiles are still very similar.

SPECTRA OF ANISOTROPIC PHASES

As seen in fig. 8. the terminal ethylene oxide gives narrow carbon peaks while the main ethylene oxide signal is broadened. The alkyl part carbon peaks are still more broadened. The terminal methyl peak is broader than the terminal ethylene oxide carbon peak, indicating that the order of the alkyl chains is higher than the order for the ethylene oxide part.

The spectrum was acquired with only 4 accumulations. This rules out the possibility of observing small isotropic domains in the anisotropic sample. Furthermore, we spun the sample with ca. 10 Hz and this would rule out any possibility of spontaneous orientation of the lamellae in the magic angle. The sample is very viscous and clearly birefringent when viewed between crossed polaroid glasses.

C O N C L U S I O N S

Chemical shifts

C13-NMR chemical shifts for the ethylene oxide chain of micellized C12E5 show low field shifts as the temperature is increased. This is interpreted as an increased stability for the trans conformations. If we compare neat C12E5 with micellized, up-field shifts are seen for the hydrated ethylene oxide, that is, more gauche conformations.

For the alkyl chain part the chemical shifts show opposite changes and they follow the ordinary pattern, that is, up-field shifts when the temperature is increased. When neat and micellized C12E5 are compared down-field shifts for the micellar C12E5 is seen.

No chemical shift changes are detected at 27°C or 60°C when the concentration is changed in the L1 phase. The hydration of the ethylene oxide chain is therefore likely to be constant.

The C13 chemical shifts for the ethylene oxide chain in different environments follow the predictions made in a recent theory of ethylene oxide conformational behaviour(28,29).

SPIN-LATTICE RELAXATION

Micellar phase

We observe a frequency dependence in the relaxation which indicates that there is some anisotropy in the fast local motions and that there is a slow motion present. Using the 'two-step' relaxation model we obtain the order parameter and the fast correlation time profiles for micellized C12E5.

Highest order is found at the C11 carbon close to the alkyl/ethylene oxide chain interface. The order parameter profile is different from that of SDS the values being lower and with no plateau. At both ends the order is low and more so for the ethoxid chain end.

The maximum in the motional restrictions is not located as for a free chain in the middle but shifted towards the ethylene oxide chain end.

Neat C12E3-5

We observe frequency-dependent relaxation for all surfactants investigated. Interpretation of the data yields fast correlation time and order parameter values. There is a higher order in neat than in micellized C12E5. The fast correlation times are slower for the end ethylene oxide group in neat compared to micellized C12E5. This is probably due to the change of the medium. The motions of terminal ethylene oxide group were not influenced by the size of the ethylene oxide chain.

Neat nonionic surfactants form thus organized liquids. The structure is unknown but the local order and mobility is not very different from that in the L1 phase.

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FIGURE CAPTION

Fig. 1. C-13 NMR chemical shift differences between micellized C12E5 at 10°C and 45°C (□) and between neat and micellized C12E5 at 27°C (●). The upper dashed line indicates zero level for the former case when the lock signal shift is taken into account. The lower dashed line indicate the zero level for the latter case when the terminal methyl is taken as internal reference .

Fig. 2. Temperature dependence of micellized C12E5 carbons. C1 is the terminal methyl group. No corrections for the shift in the lock-signal is done. The shifts are relative those at 10°C.

Fig. 3. Spin-lattice relaxation rates (at 8.45T) of some methylene groups of C12E5 in water as a function of surfactant concentration(% by weight). The terminal methyl group is denoted as C1 and the terminal ethylene oxide methylene group as C22. a) results at 27°C b) results at 6°C.

Fig. 4. C13 T1 relaxation rates of C12E5 at 43 w% in D2O as a function of field strength. ($\square$) indicates 8.5 T , ($\blacktriangle$) indicates 2.34 T and ($\bullet$) indicates 1.4 T. The temperature is 27°C. The error bars denotes +/- one standard deviation.

Fig. 5. Same as in fig.4, but at 6°C and 20 w% C12E5 in D2O.

Fig. 6. Relaxation rates for neat nonionic surfactants C12E3-6 at 27°C and 1.4 T.

Fig. 7. Relaxation rates for neat nonionic surfactants C12E4 and C12E5 at three different field strengths; 1.4 T, 2.34 T and 8.5 T. The temperature is 27°C.

Fig. 8. C13 NMR spectrum of C12E5 in a) the lamellar(27°C,) and b) the hexagonal(6°C,) phase.

Fig. 9. The phase diagram of C12E5 - water. (From ref.27)

Fig.10. Order parameters as a function of position in the chain for micellar C12E5 at 27°C.

Fig.11. Order parameters as a function of position in the chain for micellar C12E5 at 6°C.

Fig.12. Order parameter profiles for neat C12E4 and C12E5 at 27°C.

Fig.13. Fast motion correlation time as a function of carbon position in the micellar C12E5 molecule at 27°C.

Fig.14. Same as under fig.13, but at 6°C.

Fig.15. Fast motion correlation times for neat C12E4 and C12E5 at 27°C.

FIGURE 1

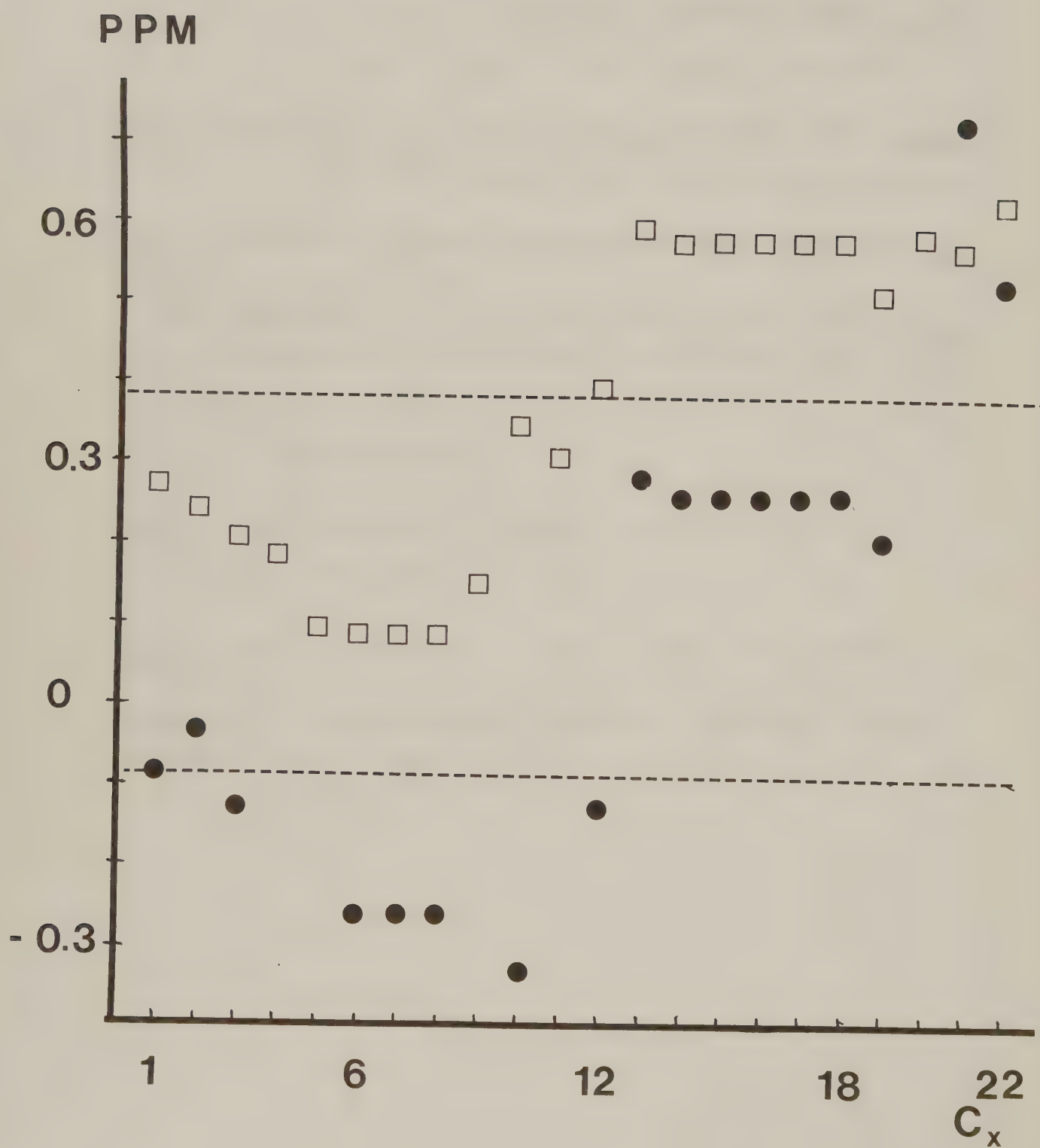


FIGURE 2

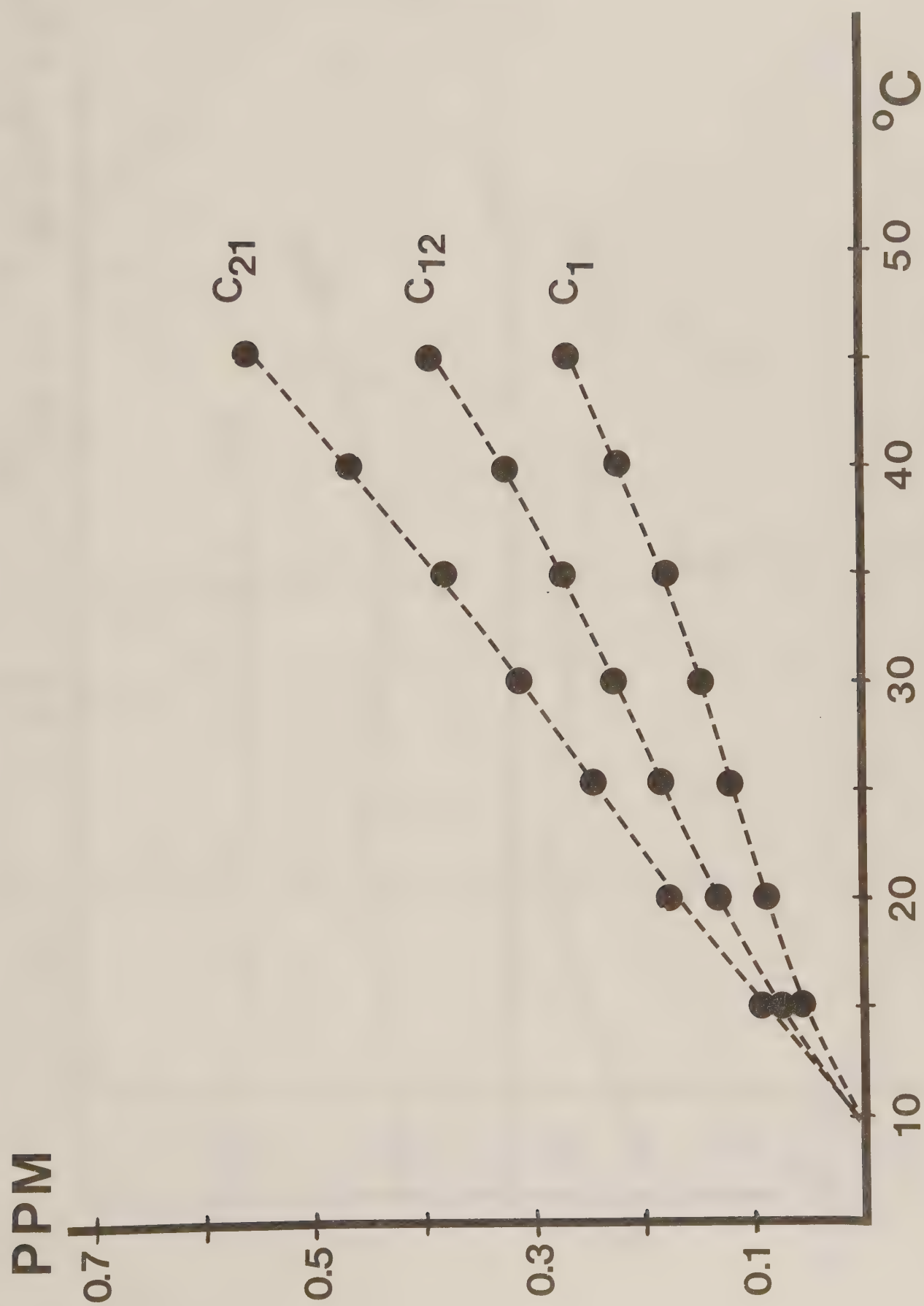


FIGURE 3 a

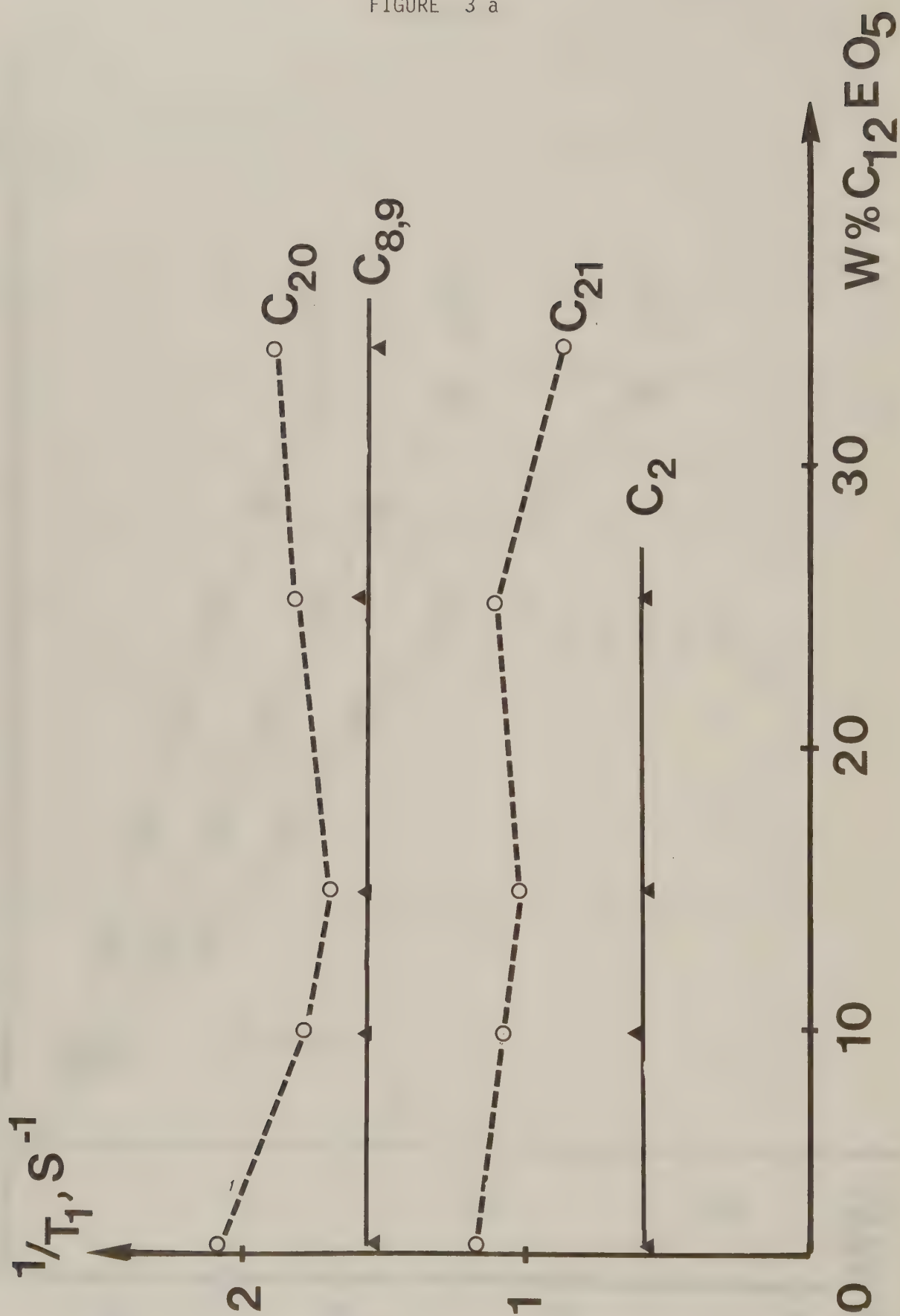


FIGURE 3 b

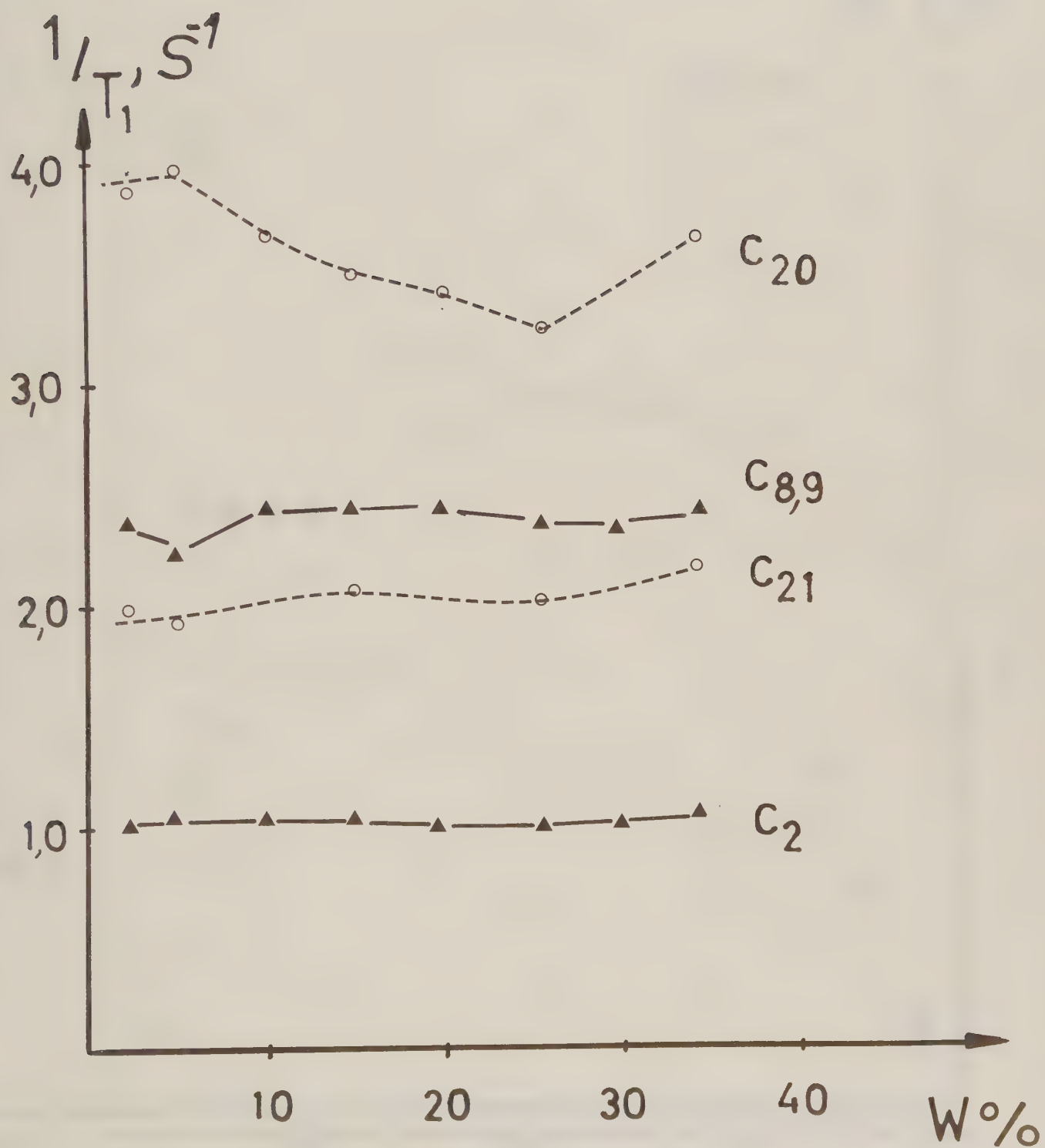


FIGURE 4

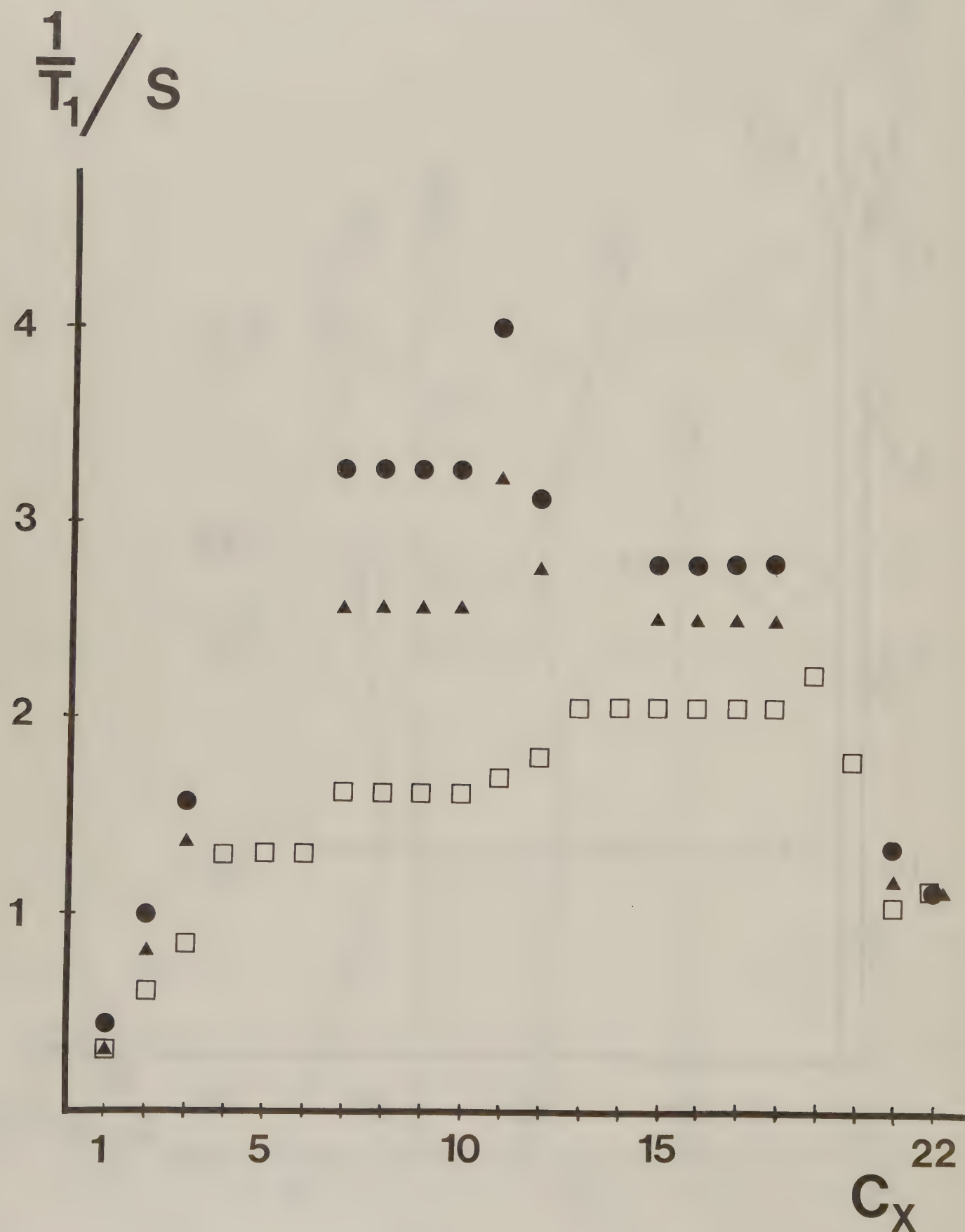


FIGURE 5



FIGURE 6

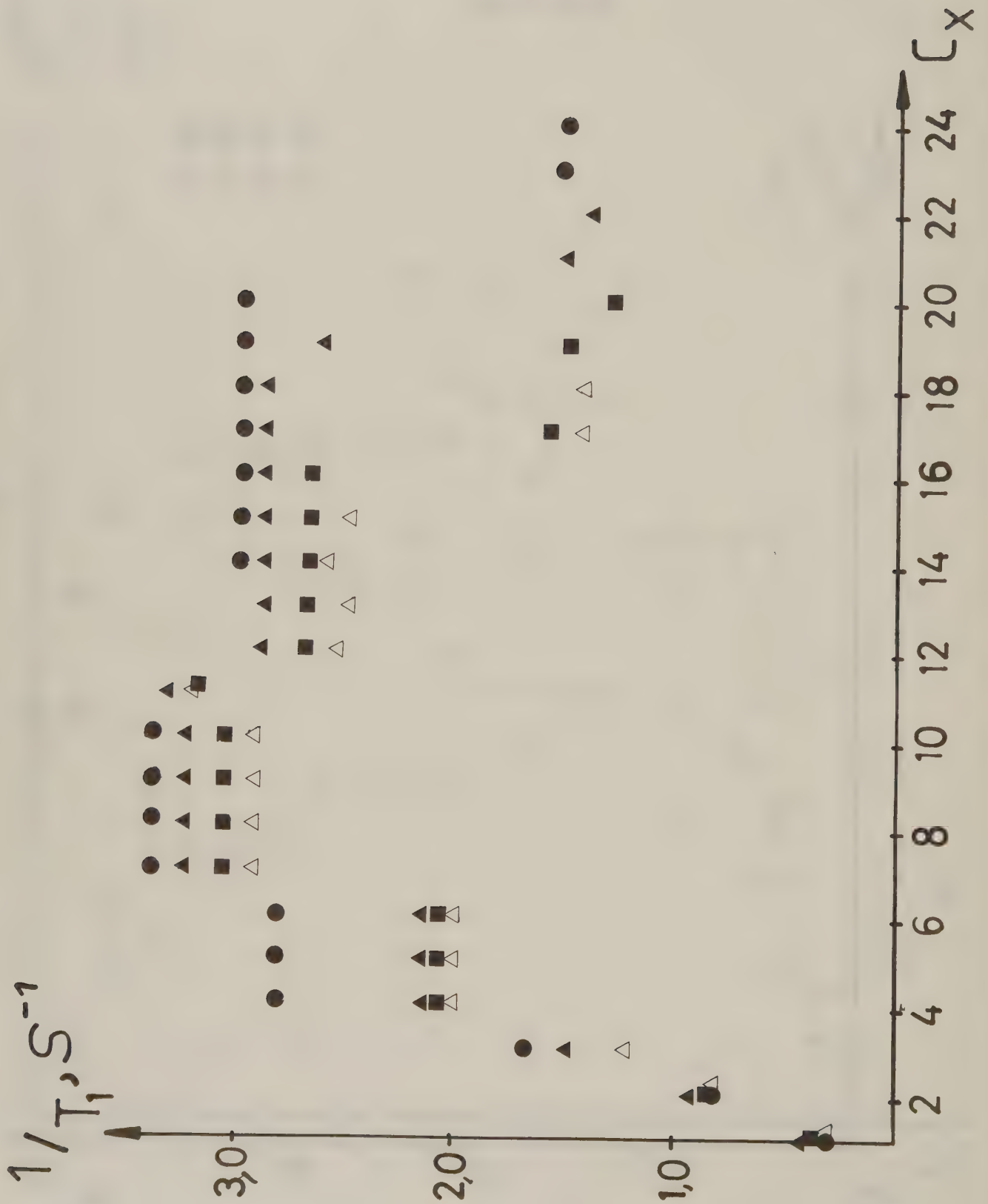


FIGURE 7

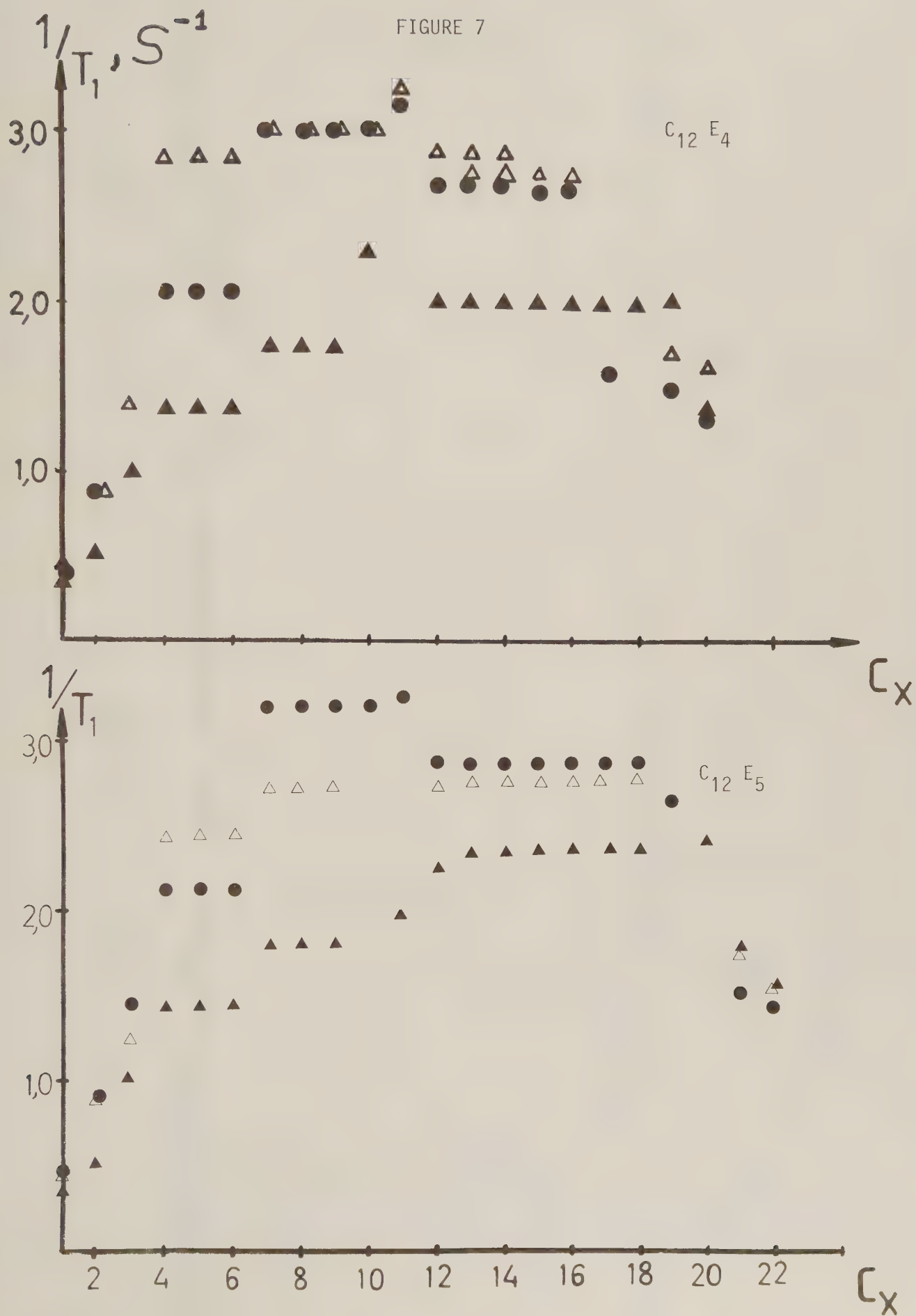


FIGURE 8 a

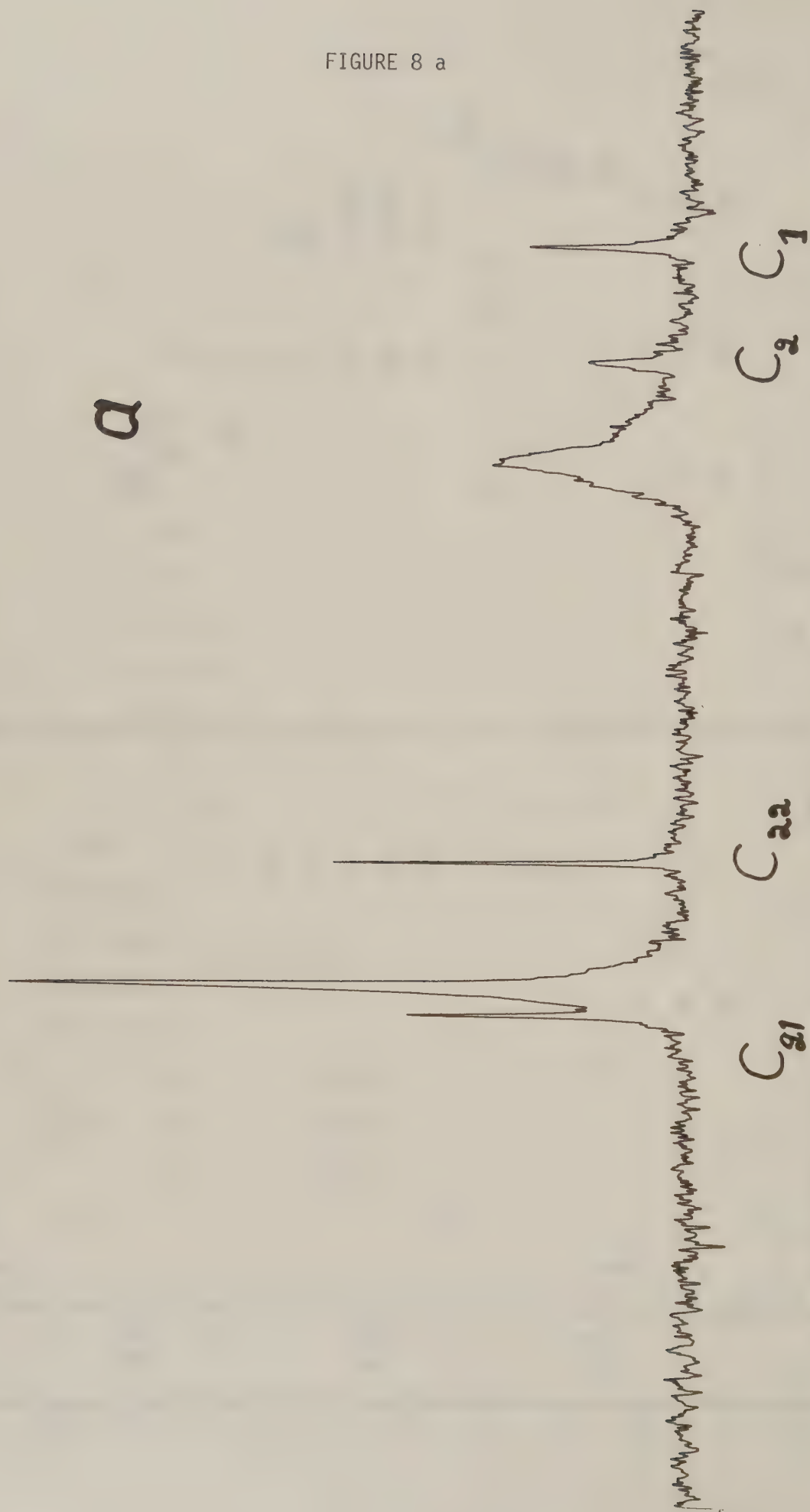


FIGURE 8 b



FIGURE 9

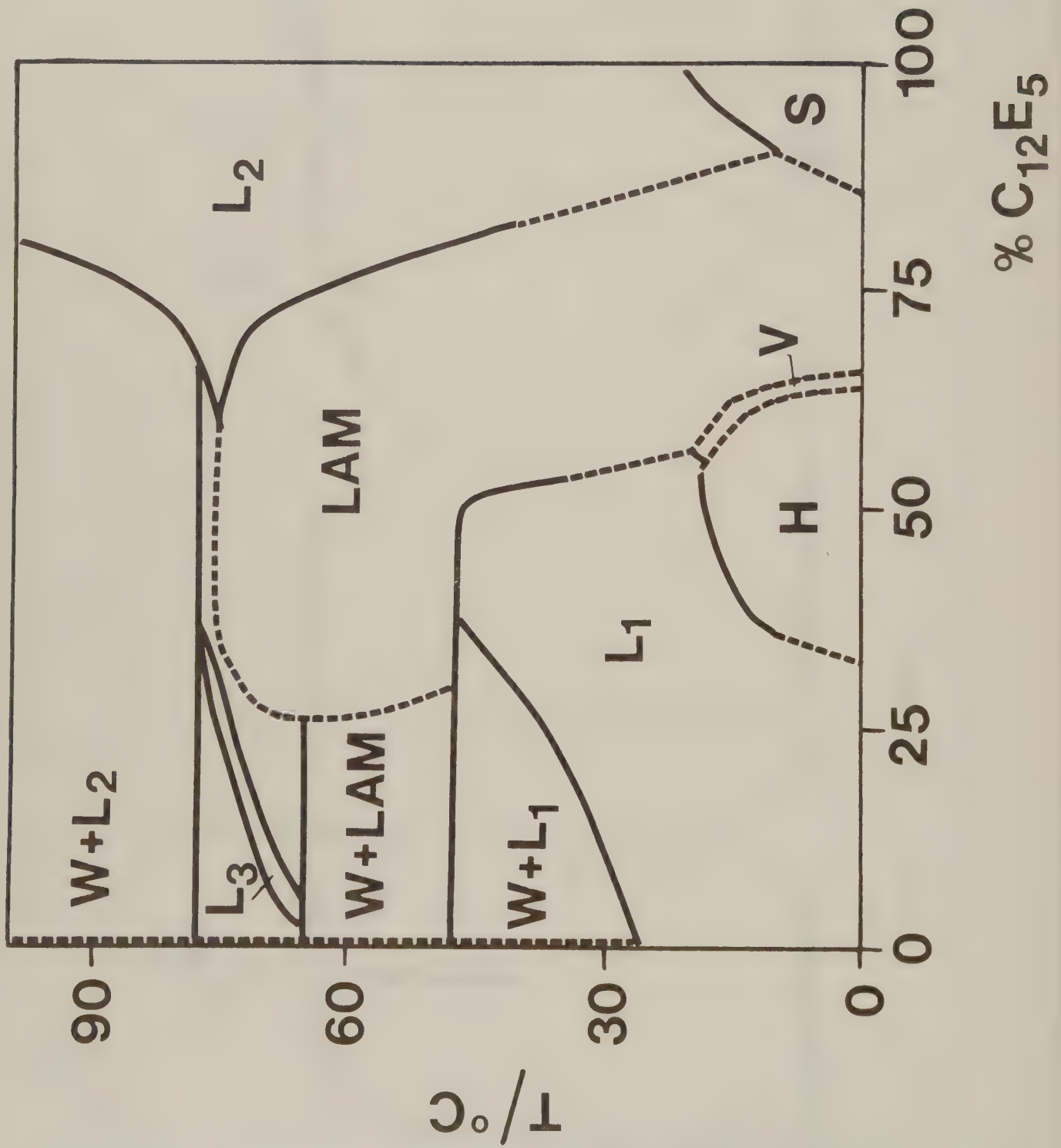


FIGURE 10

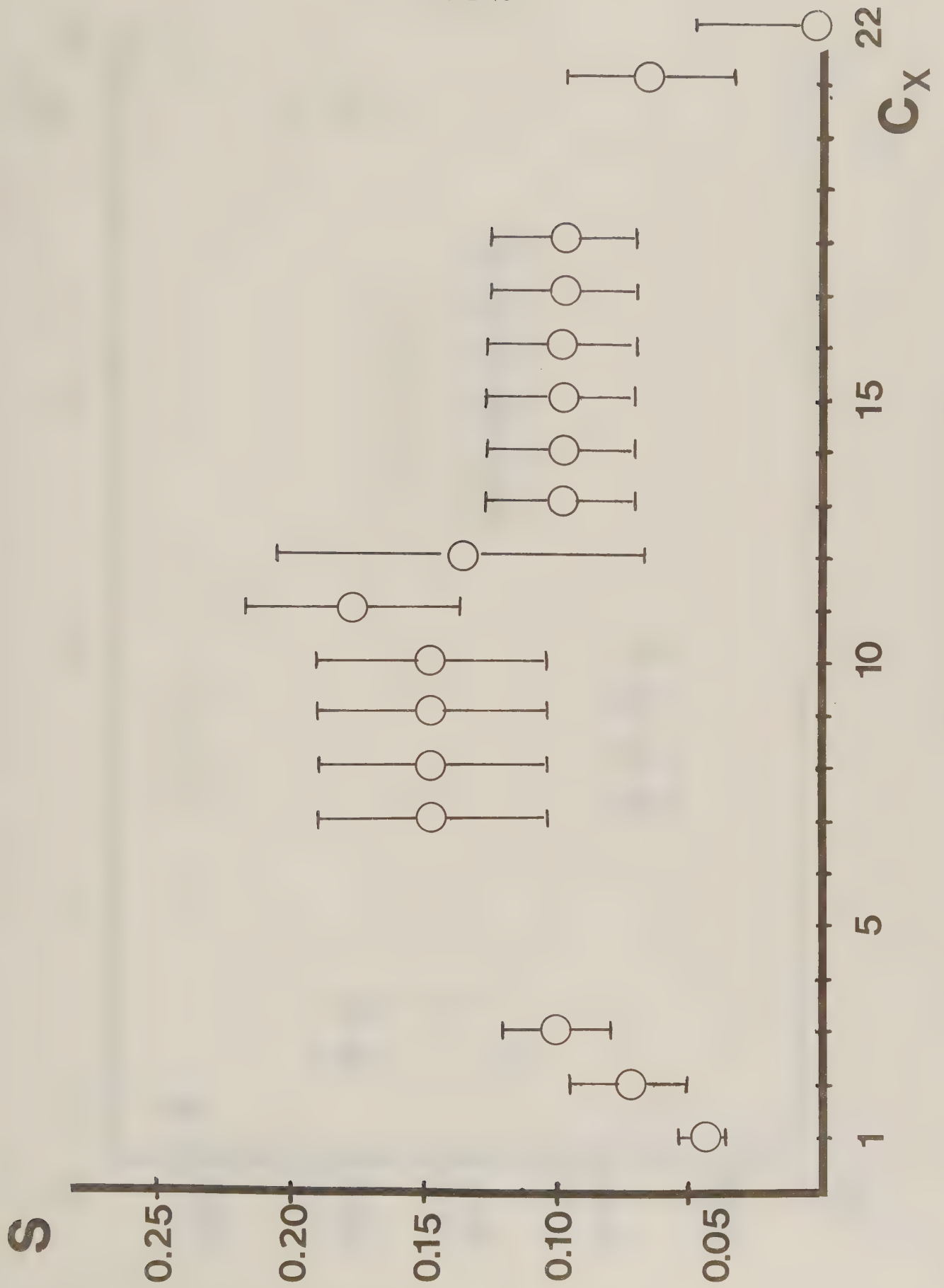


FIGURE 11

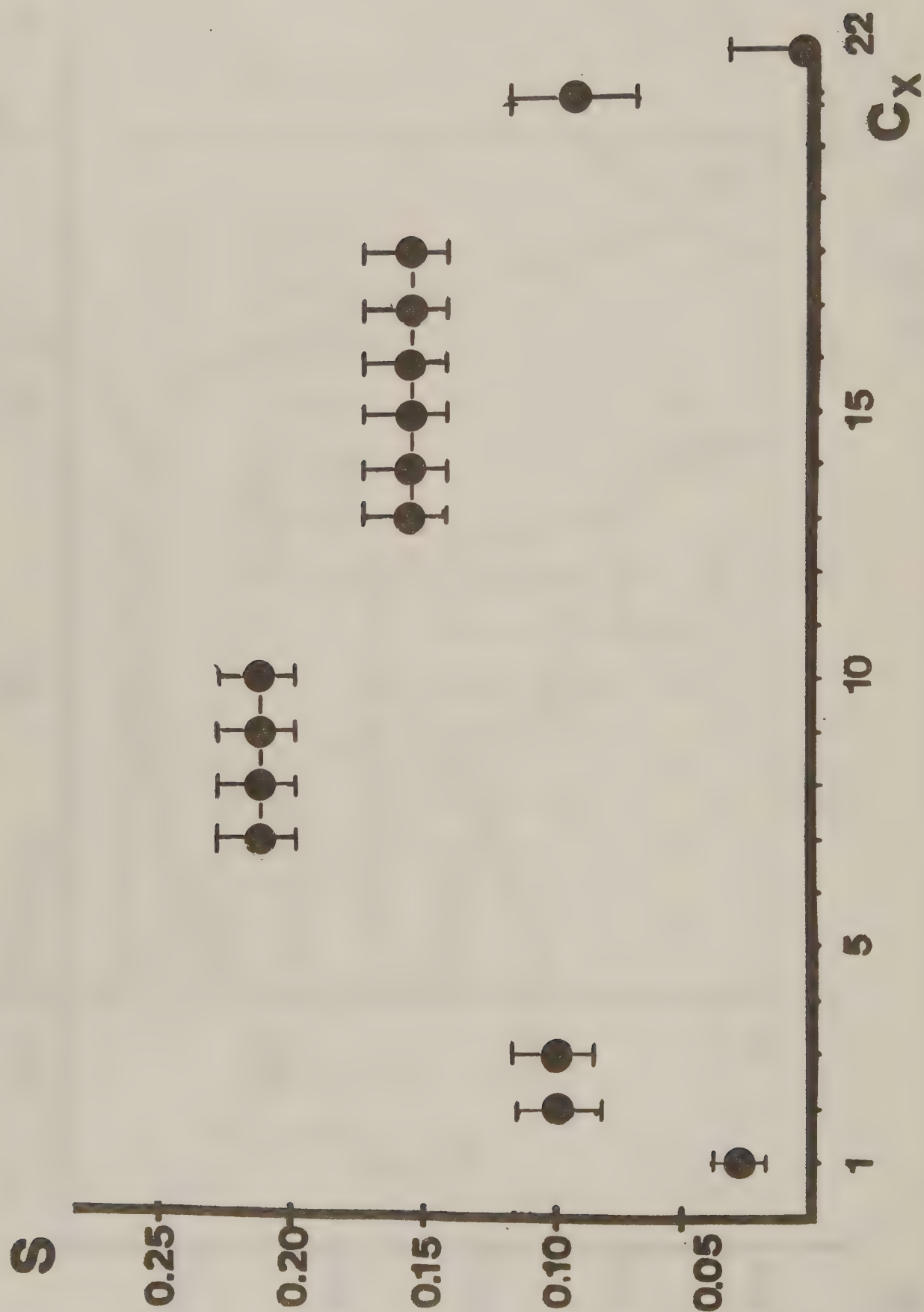


FIGURE 12 a

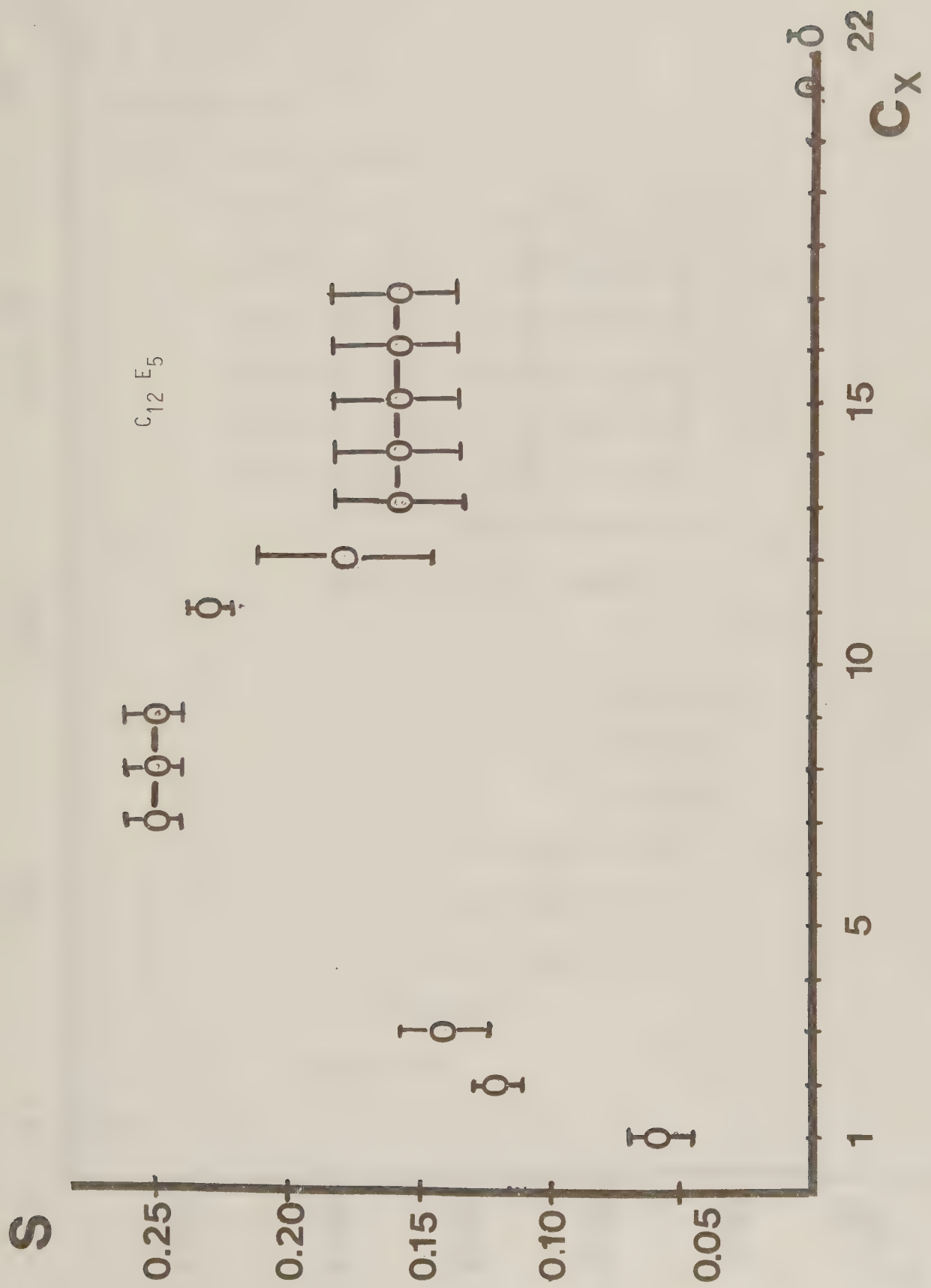


FIGURE 12 b

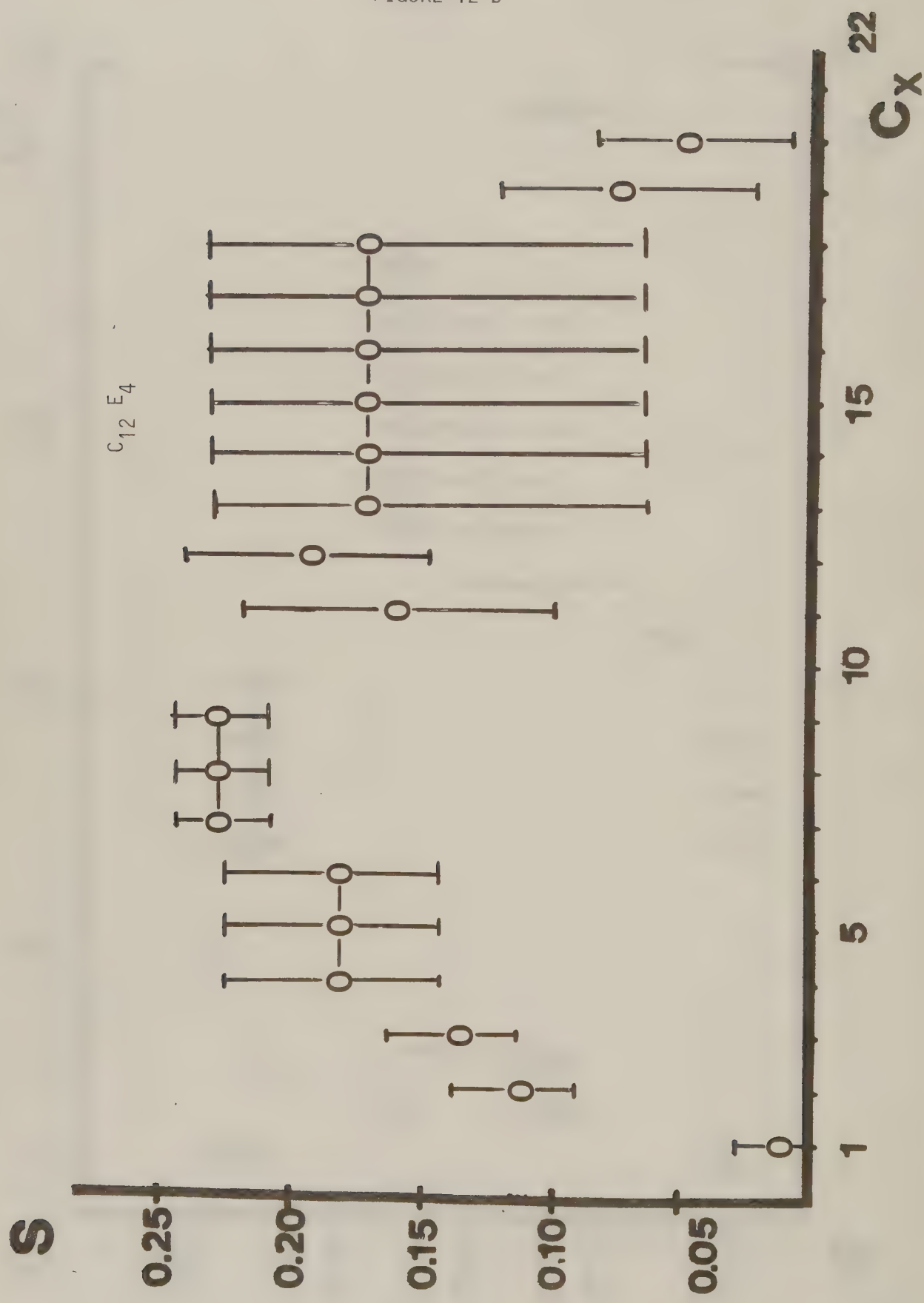


FIGURE 13

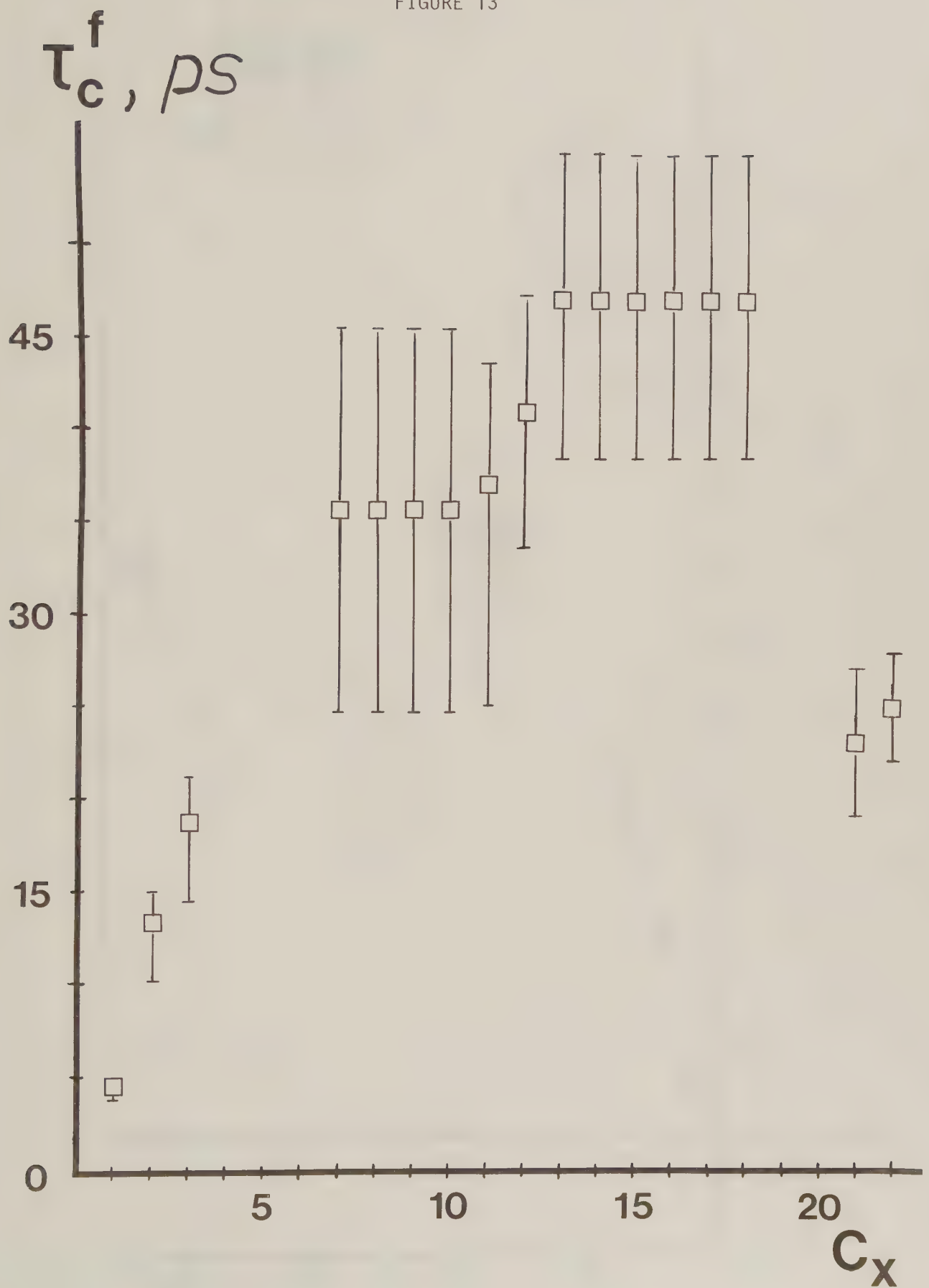


FIGURE 14

τ_c^f , PS

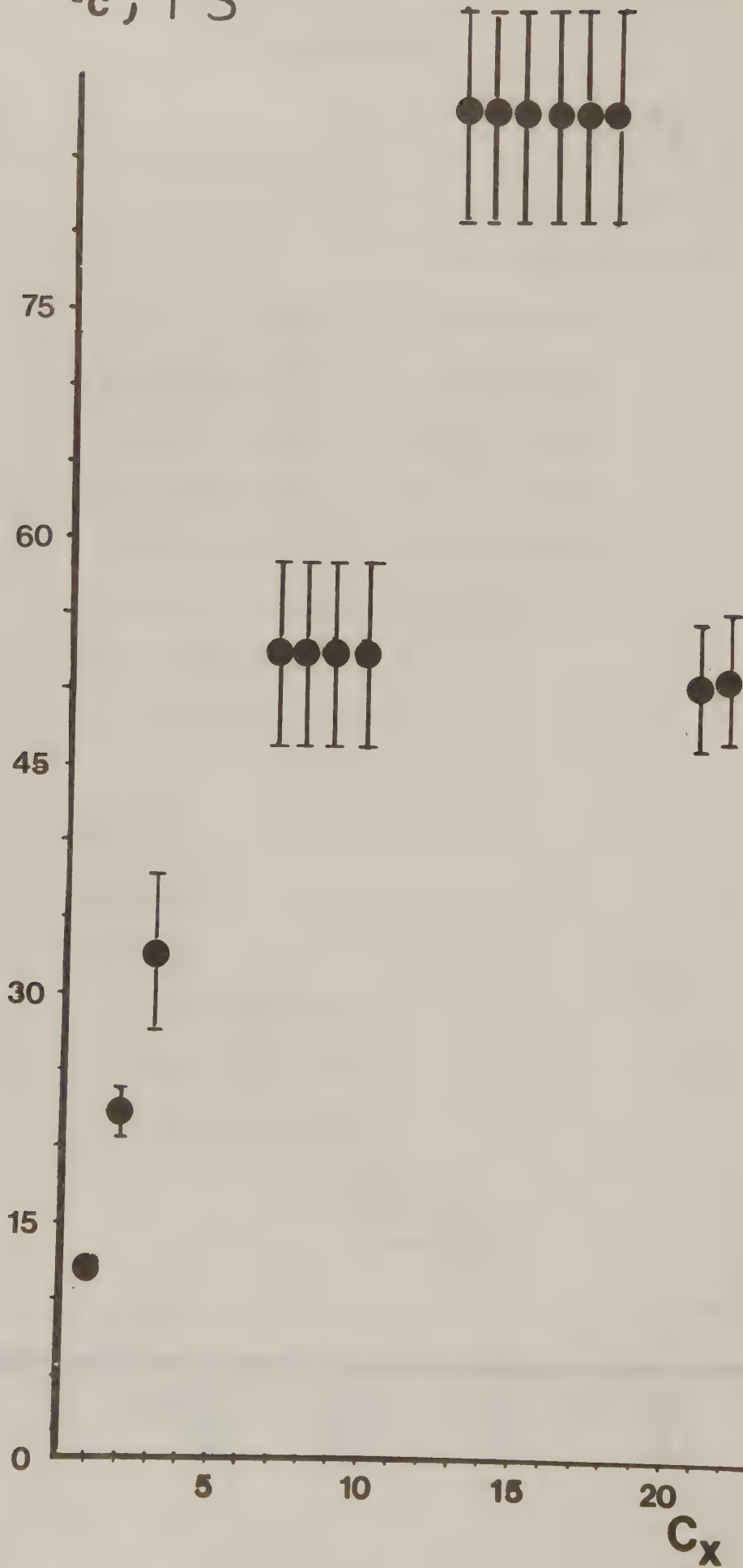


FIGURE 15 b

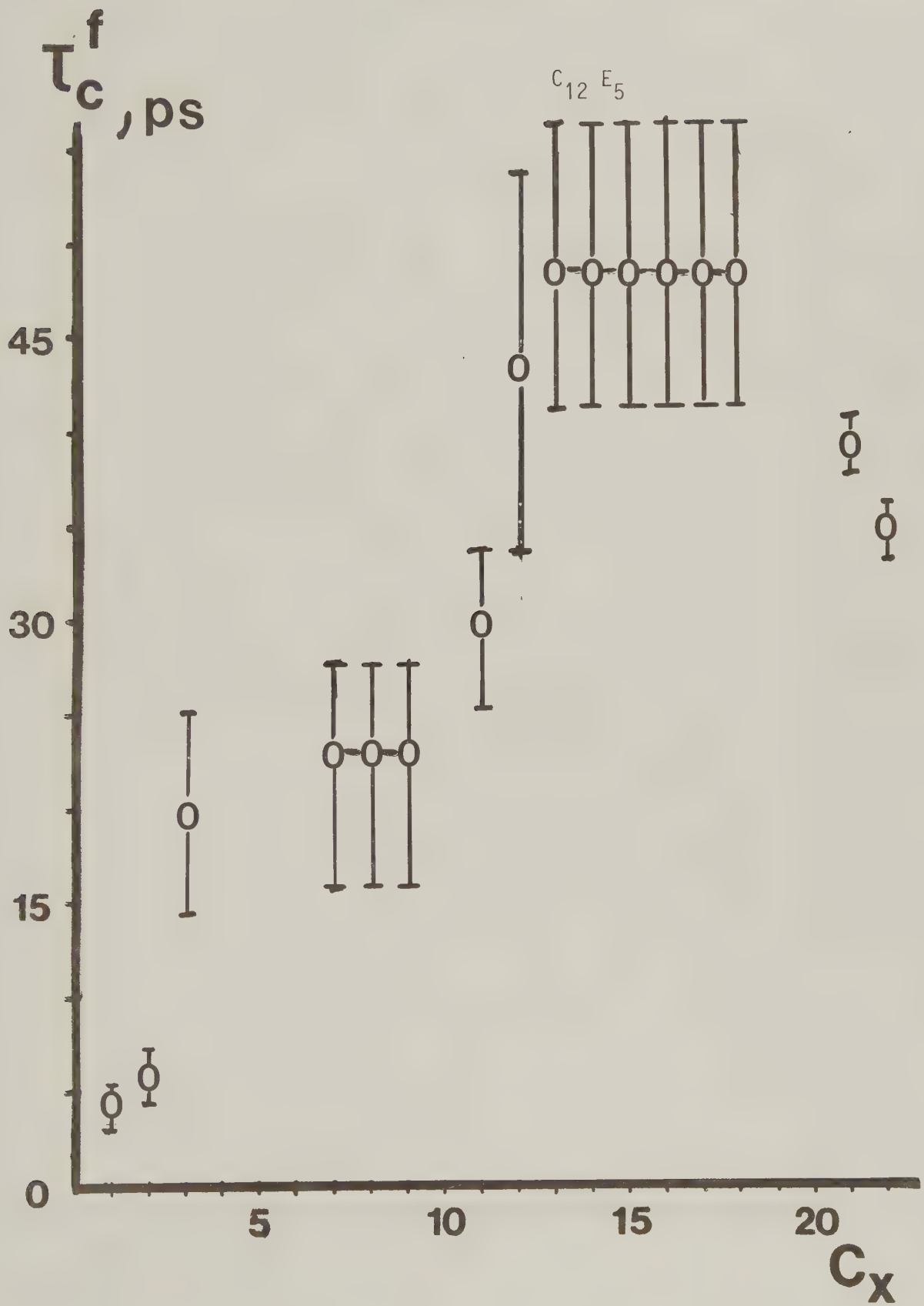
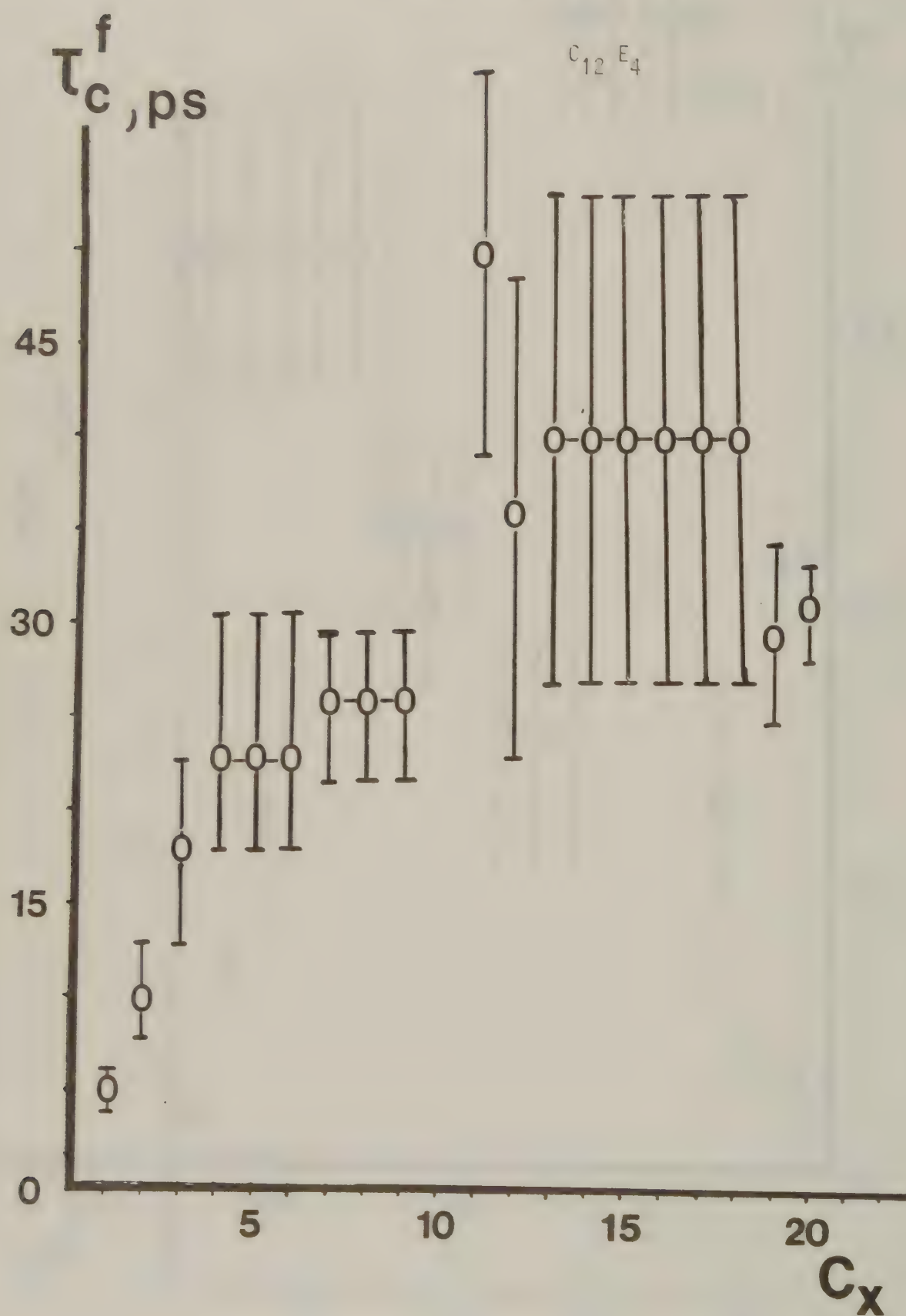


FIGURE 15 a



VII

A MULTIFIELD C-13 NMR RELAXATION AND NUCLEAR OVERHAUSER
ENHANCEMENT STUDY OF SODIUM DODECYL SULFATE MICELLES

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ABSTRACT

We have investigated the C-13 NMR spin-lattice relaxation of sodium dodecyl sulfate (SDS) in water as a function of concentration and magnetic field strength. A clear field dependence in the relaxation was found. The concentration dependence was weak in the examined region. We also determined the nuclear Overhauser enhancement at one field. Values between 1.29 and 1.92 were found for the different methylene and methyl carbons.

A two-step relaxation model was used to interpret the relaxation rates. Thus, we have obtained information on the surfactant hydrocarbon chain order and mobility in addition to a slow correlation time associated with the overall motion of the micelle.

We have compared experimental order parameters, extracted with the same technique, of SDS, dodecyl pentaethylene oxide (C12E5) and dodecyl tri methyl ammonium chloride (DOTAC) micelles. Our SDS order parameters were also compared with those obtained from simulations and the similarities strongly supports the validity of these simulations. The order is quite similar for SDS and DOTAC but slightly lower for C12E5. No comparison could be made with experimental order parameters of SDS in anisotropic phases due to the lack of data. However, we have compared order parameters of potassium laurate in lamellar and hexagonal phase with our SDS results and theoretical data. Thus, we observe that there are large differences between

order in the lamellar and the micellar phase. The hexagonal order parameters are for all but the first carbon lower than the micellar ones.

The influence of the head group on the fast local motions was also studied. Again SDS and DOTAC values were similar but for C12E5 longer correlation times (slower motions) were found.

INTRODUCTION

The structure of surfactant micelles has been explored and debated ever since they first were realized to exist. Still, new information is possible to obtain since theory(1) and experimental techniques¹ are improving. Particularly interesting is the comparison(2,3) of theoretical and experimental results.

We have chosen to investigate the sodium dodecyl sulfate micelle because it has been one of the most studied systems(4-19). For the anisotropic phases, experimental results are available for the lamellar(20) and hexagonal(20, see also data in ref. 2) phases of potassium dodecanoate (KD) in water. Order parameters for some surfactant dodecyl chains are available both from experiments on micelles(26,27) and from simulations(2,3,23-25).

The aim of this work was to determine fast correlation times and order parameters for micellar SDS. These results are then compared with values, obtained by the same technique, for other micellar dodecyl chain surfactants(26,27). Furthermore, order parameters obtained in simulations are compared to our experimental results. The micellar SDS order parameters are also compared with ^2H -NMR order parameters of KD in lamellar and hexagonal phase as well as theoretically calculated.

EXPERIMENTAL SECTION

The sodium dodecyl sulfate was obtained from BDH and it was of highest purity. The heavy water was from Norsk Hydro. All measurements were done at 28°C and the NMR sample tubes were provided with vortex plugs. The relaxation times were determined by the fast inversion recovery technique (FIRT)(28). At the highest field two-level decoupling 10 was used to avoid heating during the decoupling. The intensity data from each experiment was treated by a three parameter fit to determine the relaxation time. The error bars (90% confidence intervals) given refer to this fit. Additional errors associated with other sources are not included. The nuclear Overhauser enhancement (NOE) was measured at the highest field (8.45 T) with the dynamic nuclear Overhauser technique (DYNOE)(29). We checked the DYNOE experimental results by comparing the spin-lattice relaxation (T_1) from this experiment with those from a FIRT experiment at the same field. The agreement was within 10 %.

We used the following spectrometers: Jeol FX-60 (1.40 T), Varian XL-100 (2.34 T) and Nicolet-360 (8.45 T).

The assignment of SDS was done according to Cabane(8). In literature three more assignment suggestions were found(9-11).

RESULTS

In figure 1. we show the relaxation rates for some of the methylene groups as a function of SDS concentration and field strength. A quite weak concentration dependence is seen.

We observe a markedly field dependent relaxation, the field dependence decreasing towards the terminal methyl group. This seems to be a general observation for aggregated surfactant systems(26,30-35).

In table 1. we list the NOE and relaxation rate values obtained at the different fields at a fixed concentration. The relaxation values are taken from the relaxation vs. field and concentration plots such as those shown in fig. 1. This procedure increases somewhat the accuracy of the relaxation values. The values in table 1. are used in the interpretation of the relaxation rates and the nuclear Overhauser enhancement.

Table 1. NOE and R1 (1/T1) values at different fields for 20 w% SDS in D2O. The values for the terminal methyl are converted to those for a methylene group by multiplying with the factor 2/3. R1 is expressed in s⁻¹.

Carbon no	NOE(8.45 T)	R1(8.45 T)	R1(2.34 T)	R1(1.40 T)
1	1.36	.84	1.82	2.95
2	1.368	1.05	2.44	3.03
3	1.29	1.05	2.30	2.95
4,9 (a	1.42	1.09	2.38	2.87
5,6,7,8 (a	1.36	1.16	2.49	2.97
10	1.438	.64	1.38	1.74
11	1.70	.44	.89	1.08
12	1.92	.173	.244	.293

a) not resolved at the lowest field (1.4T).

A complete table of experimental data is available upon request.

DISCUSSION

From fig. 1. it is evident that the concentration dependence of T1 is low well above the CMC. This seems generally to be the case for C13 T1 relaxation in micellar solutions. There are some indications that this would also be true in the anisotropic phases(36).

Several experimental techniques(6,11,12,14-17) have been used to study the size and shape of SDS micelles. Most of them are concerned with the size and shape at relatively low surfactant concentrations and in the presence of salt. There are, however, some indications that the micelle is growing as the concentration is increased(14,15). The aggregation number would then increase from the initial value of ca. 60 to about the double when going from the critical micelle concentration to 0.8 M.

For several surfactant systems the Wennerstrom two-step model(30) has been used to interpret the relaxation data. The principles of its use for C13 relaxation are described in previous publications(26,30-32).

If we fit our data to the two-step model we obtain three parameters, the fast correlation time (in ps) for the fast local motions (like gauche/trans isomerism), the order parameter S (directly comparable to that determined from deuterium NMR splittings in lamellar phases) characterizing the anisotropy of the fast motion for each carbon, and a slow overall motion (in ns) common to all carbons.

The order parameter

In fig. 2. the order parameters are shown. A 'plateau'-like profile is found. This is similar to profiles obtained for other long chain surfactants in the lamellar phase experimentally and by simulation(37).

However, the profile indicates that the forces between the alkyl chains dominate so that the changes in curvature and head group area do not change the order parameter profile so much. It is believed that for alkyl chains the possible alkyl chain conformations are restricted mainly by the available space. For shorter alkyl chains the area changes at the head group will have larger effects on the order parameter values and the profile since the forces between the alkyl chains are reduced(31).

Micellar order compared to lamellar and hexagonal

There is, unfortunately, no experimental order parameter values of SDS in lamellar or hexagonal phase. Thus, we will not be able to compare the order parameter profiles for SDS in different aggregate structures, but we are able to compare our results with ^2H -NMR order parameters of potassium dodecanoate in lamellar and hexagonal phase. This is done in fig. 3a-c. Theoretical values of Szleifer(3) et al. are also included. (The potassium dodecanoate data was originally taken from ref. 2 and 20 by Szleifer(3) and are now here completed by our data)

The much higher temperature of case b) must be taken into consideration when comparing. Increasing the temperature about 20°C will lower the values with approximately 15%(26).

In the micellar phase SDS, DOTAC and the theoretical values agree besides for the sulfate α -carbon. This might be a consequence of the different head group. For the hexagonal phase, taken into account the 15% lowering of the SDS values, there are no larger differences besides for the low value of the SDS α -carbon. For the lamellar phase we find substantial differences and most of the SDS values are lower. These results demonstrate the similarities between the micellar and hexagonal aggregate alkyl chain order and the different order of the lamellar aggregate.

The effect of changing the head group on the order parameters

It is of interest to compare the here deduced order parameter values with order parameters, obtained with the same technique, for surfactants with the same alkyl chain length but with a different functional group. This is done in table 2.

Table. 2. Order parameter values for different micellar dodecyl surfactants. The accuracy is given within brackets as a 90% confidence interval. The dodecyl penta ethylene oxide (C12E5) data is from ref.27 and the dodecyl trimethyl ammonium chloride (DOTAC) data is from ref.26.

carbon no	SDS (20W%, 28C)	C12E5 (45W%, 27C)	DOTAC (20W%, 27C)
1	.168 (.165-.169)	.141 (.128-.166)	.23 (.22-.24)
2	.185 (.180-.191)	.185 (.169-.189)	.22 (.19-.23)
3	.184 (.179-.188)	.15 (.129-.167)	.21 (.20-.23)
4	.177 (.174-.183)	.15 (--)	.19 (.18-.21)
5	.182 (.180-.194)	.15 (--)	.19 (.17-.21)
6	.182 (--)	.15 (--)	.19 (.16-.20)
7	.182 (--)	. (--)	.18 (.16-.20)
8	. (--)	. (--)	.17 (.15-.20)
9	.177 (.174-.183)	. (--)	.14 (.10-.14)
10	.136 (.130-.141)	.105 (.09-.12)	.12 (.10-.14)
11	.101 (.094-.103)	.075 (.068-.086)	.08 (.03-.11)
12	.043 (.041-.047)	.03 (.01-.03)	.05 (.02-.06)

Table 2. indicates that the order is lowest for the nonionic surfactant, but the differences are rather small. Some care has to be taken since the nonionic study did not include NOE data and thus the slow correlation time was not so well defined as for the others. Also, since the exact aggregate form is not known (flexible rods might be one possibility) the order parameter values might change somewhat. In case of long rods order parameter values would increase by the square-root of $4/3$. The higher concentration of C12E5 is not influencing the comparison since there was no concentration dependence in the relaxation well above the critical micelle concentration.

Comparison with simulations

We are also able to compare order parameters from Gruen's simulations(2) with our experimental values, which is done in table 3.

Table 3. Comparison between experimental and simulated order parameters

CARBON NO	EXPERIMENTAL	SIMULATED
	(SDS, 28°C)	(40C, ref. 2)
1	.168	.207
2	.185	.188
3	.184	.190
4	.177	.184
5	.182	.177
6	.182	.165
7	.182	.160
8	.182	.146
9	.177	.135
10	.136	.118
11	.101	.101
12	.043	.03

The difference in order parameter values between 40C and 28C will be about 5% (increase) as judged from experimental values(26). We then see that there is a good agreement between these two methods. This greatly supports the validity of this single chain simulation. Also other simulations have been reported. A more detailed analysis of them can be found in ref.23.

The fast local motion

In figure 4. the correlation times of the fast local motions (mainly gauche/ trans isomerism) for the micellar SDS is shown. We observe a profile that clearly shows that the alkyl chain mobility is slowed down at the polar head as compared to a free chain where both ends have the same mobility. The maximum in the fast correlation time is not located at the α -carbon, which indicates that the polar head group does not act as a fixed wall. The slightly higher mobility for the β -carbon than for the α -carbon has been observed also for other dodecyl surfactants (27,26). It is possible, that the effect of some protrusion could explain this. However, if we start with a free chain and slowly increase the anchoring of one end, then the minimum of mobility in the middle of the chain(38) will move towards the end that is anchored. It is conceivable that the SDS molecule in micelles is in an intermediate state between an all free chain and a chain with one fixed end, and therefore shows the observed fast motion correlation time profile.

It is, however, evident that the local motions are very fast and resemble those found for alcohols(39) with the same alkyl chain length. The interior of a micelle is thus very liquid like.

The effect of changing the head group on the fast motion correlation times

If we compare the fast motion correlation time profiles and values of different dodecyl chain surfactants in micelles we find that the nonionic ethylene oxide group has the largest influence (see table 4.).

Table 4. Fast motion correlation times (in ps) for different dodecyl chain surfactants when aggregated into micelles. The experimental conditions are the same as in table 2.

CARBON NO	SDS	C12E5	DOTAC
1	12.8	40.6	15.9
2	16.6	36.1	16.8
3	15.7	34.8	20.5
4	18.1	34.8	20.6
5	18.6	34.8	20.5
6	18.6		22.5
7	18.6		20.8
8	18.6		20.0
9	18.1		17.7
10	10.5	18.6	13.8
11	8.2	13.3	11.3
12	3.6	4.3	4.6

The values above indicate that the nonionic surfactant alkyl chain motions are slower than the others. The reason would be that the penta ethylene oxide (E5) head group is much larger and it would then influence more. The much smaller difference between DOTAC and SDS fast motion correlation times can be seen in the light of the comparable head group sizes. Also the insensitivity of the spin-lattice relaxation to changes in concentration indicates that the fast local motions are less dependent on the actual aggregate structure (and electrostatics) but more determined by the head group physical size and hydrogen bonding to the head group.

It is tempting directly to compare fast motion correlation times for hydrocarbons with table 4. Since these correlation times are effective correlation times and we do not know their different contributions it is dangerous. For hydrocarbons molecular tumbling and gauche-trans isomerism will be at the same fast time scale. For aggregated surfactants the contribution from molecular tumbling will certainly be changed as for alkyl chain alcohols due to hydrogen bonding. Nevertheless, the ps time scale of the fast motion correlation times clearly demonstrate the liquid-like micellar interior.

The slow motions

The slow motion correlation time was determined to be 3.3 ± 0.5 ns, and it was quite well determined from the experimental results as table 5. indicates.

Table 5. Error sums as a function of the slow motion correlation time.

The error sum is defined as the sum taken over all squares of the differences between the observed and the calculated values (of the relaxation rates and NOE:s) divided by the square of the observed value. For details see ref.26.

<u>Slow correlation time(ns)</u>	<u>Error sum</u>
.9	.748
1	.676
2	.204
3.27	.042
4	.072
5	.169
6	.286
10	.669

It has earlier been suggested that the slow overall motion consists of two parts, one arising from the tumbling of the aggregate and one from lateral diffusion of the surfactant monomer around the aggregate. The aggregate tumbling is described by the Debye-Stokes-Einstein equation

$$\tau_c^R = \frac{4\pi\eta R^3}{3kT}$$

where R is the aggregate radius and η is the viscosity of the medium, k is the Boltzmann constant and T is the absolute temperature. The tumbling of the micelle is expected to be quite insensitive to inter micellar interactions (except for long rods).

The lateral diffusion correlation time is given by

$$\tau_c^L = \frac{R^2}{6D_L}$$

where D_L is the lateral diffusion coefficient.

These two correlation times give the effective slow motion correlation time (τ_c^S) and if the two motions are independent

$$\frac{1}{\tau_c^S} = \frac{3kT}{4\pi\eta R_A^3} + \frac{6D_L}{R_D^2}$$

If we assume that just the rotational process occurs we get an aggregate radius of 15.3 Å, which is some too low. The hydrocarbon chain length(40) is 15.4 Å and including the polar group we will have a total length of at least 18 Å. If we take that value and calculate the lateral diffusion coefficient of SDS we obtain $6 \pm 2 \times 10^{-11} \text{ m}^2/\text{s}$. For SDS we found some values of the diffusion coefficient that were measured in the gel phase (at 25°C) and in the lamellar phase (at 88°C)(42), but they seem to be unrealistically fast. For sodium octyl sulfate the lateral diffusion coefficient has been determined in the lamellar phase and it was $3.5 \times 10^{-11} \text{ m}^2/\text{s}$ (at 25°C)(41). Thus, we conclude that we have got a realistic lateral diffusion coefficient for SDS in micelles and that both the tumbling and the lateral diffusion contributes to the observed slow motion.

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FIGURE CAPTION

Fig. 1. C13 NMR spin-lattice relaxation rates of micellar SDS as a function of field strength and concentration for three different methylene groups in the chain. Numbering of the carbons is from α -CH₂ (1) to ω -CH₃ (12). The temperature is 28 C

Fig. 2. The order parameter profile of micellar SDS (20 w%) at 28 C. The error bars correspond to a 90 % confidence interval.

Fig. 3a-c. Order parameter values of micellar SDS (filled circles) at 28C compared with a) micellar DOTAC(26) (open circles) and theoretical(3) values (open squares) at 27C b) hexagonal KD(20) (open circles) and theoretical(3) values at 50C. c) lamellar KD(20) and theoretical(3) values at 31C.

Fig. 4. SDS fast motion correlation time profile at 20W% and 28C. The error bars correspond to a 90% confidence interval.

FIGURE 1

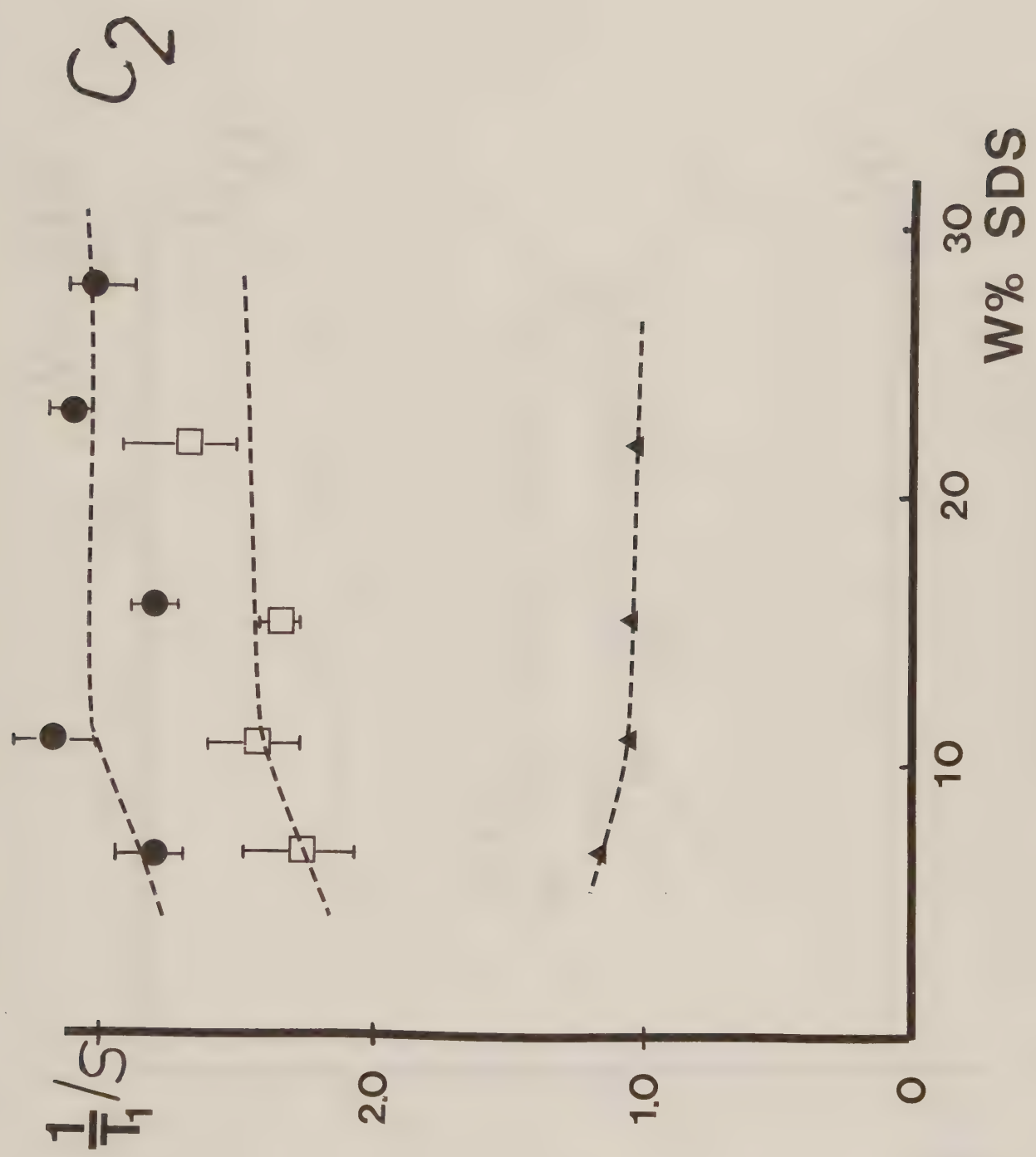


FIGURE 1

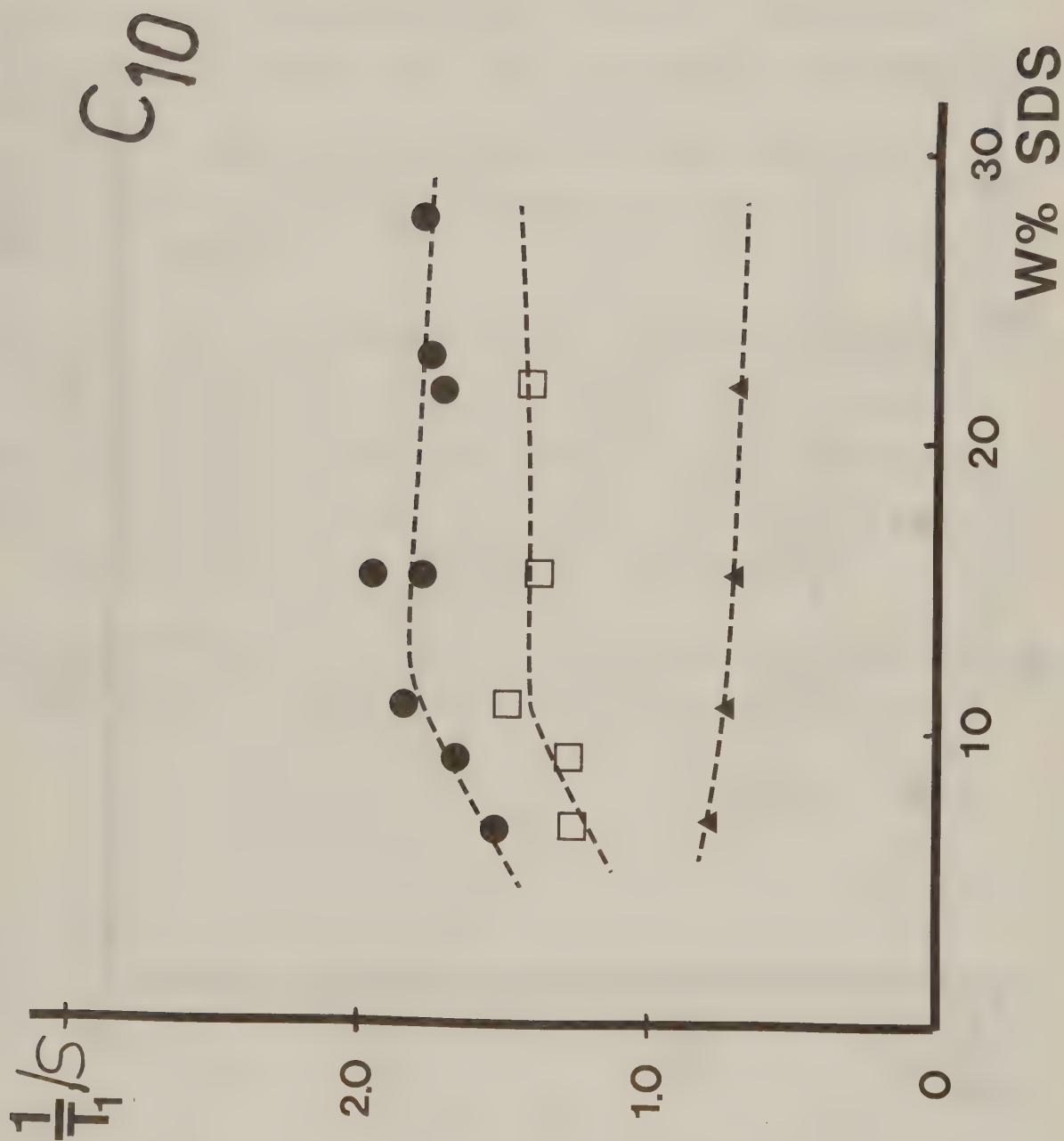


FIGURE 1

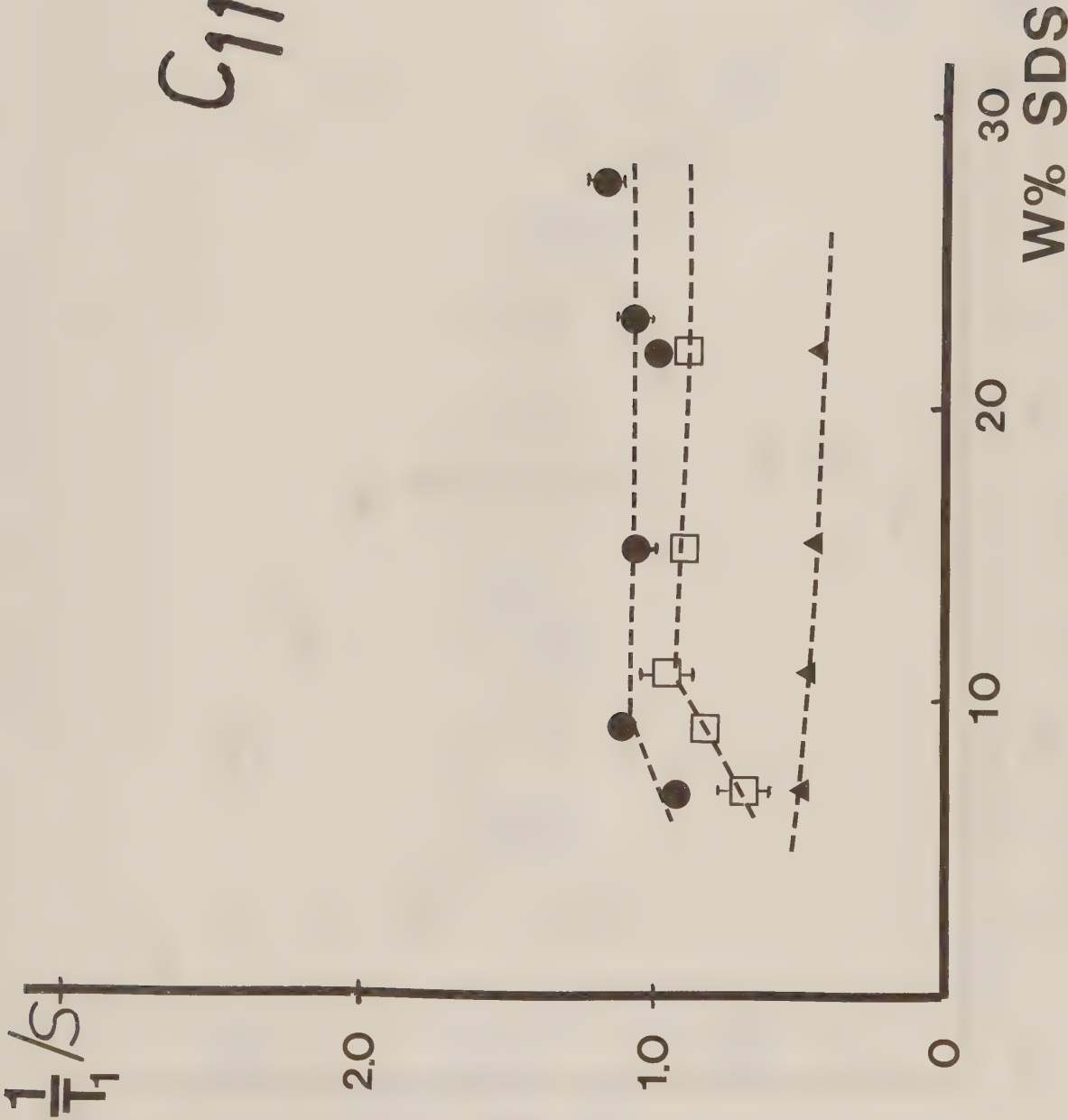


FIGURE 2

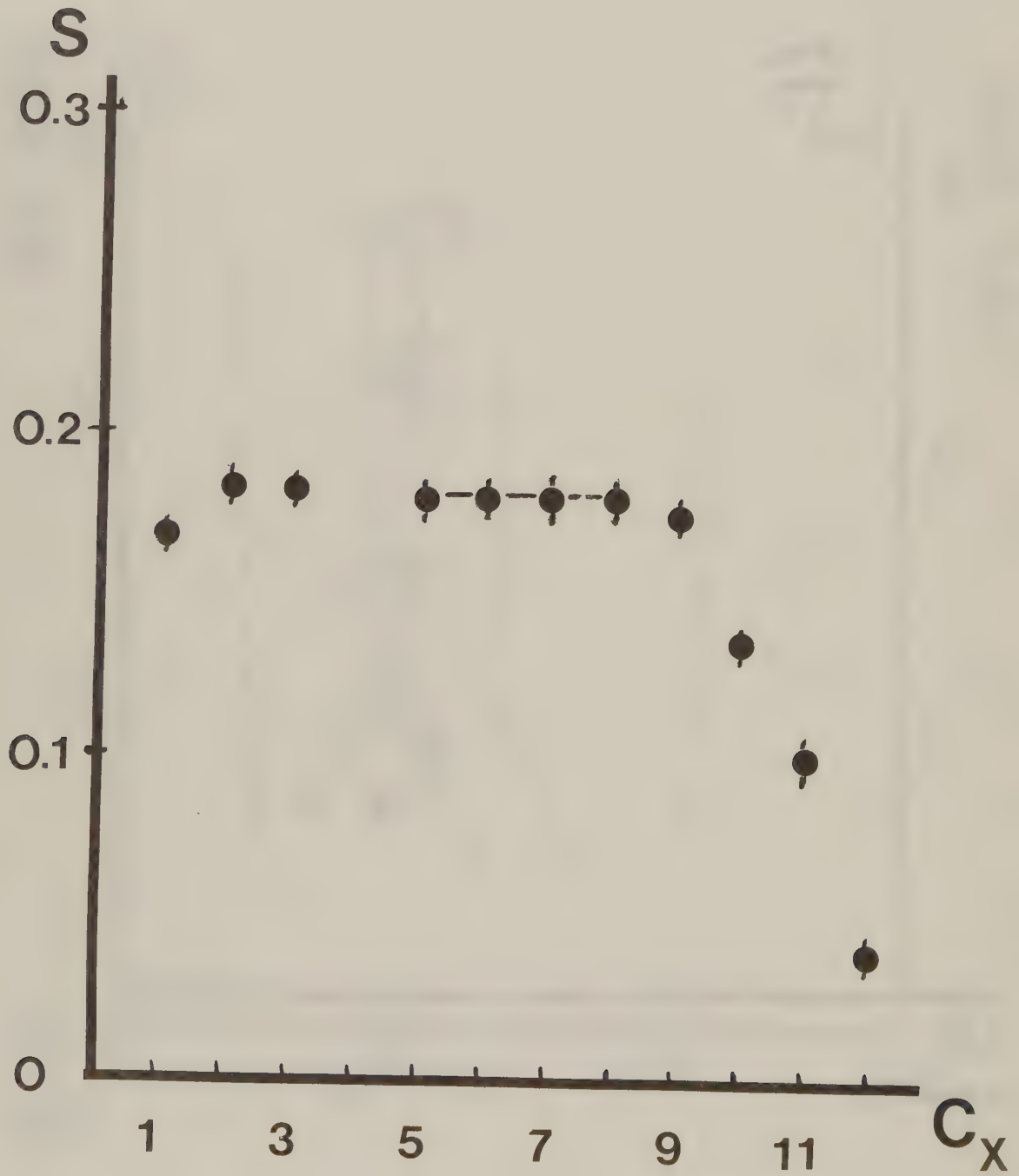


FIGURE 3 a

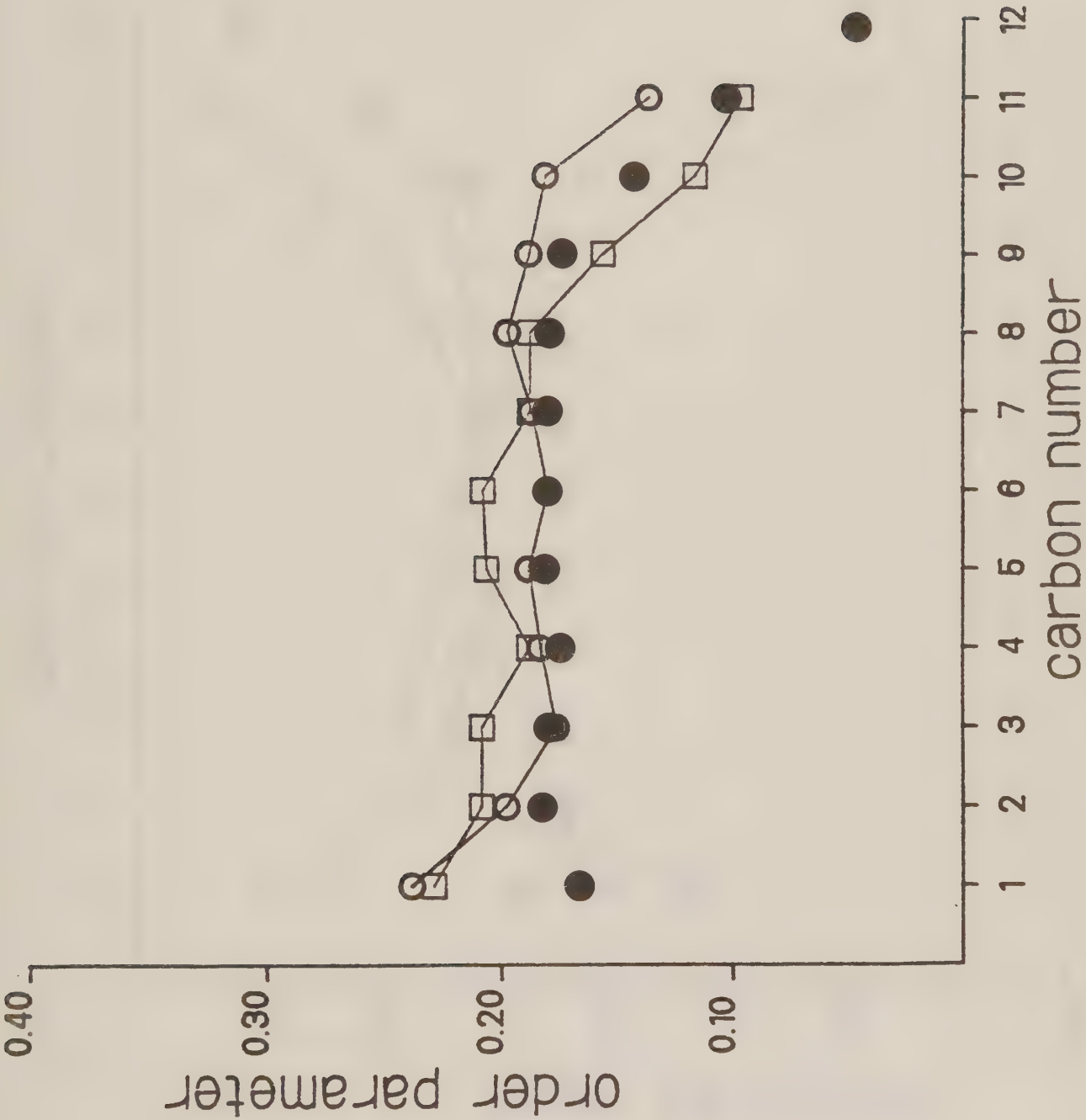


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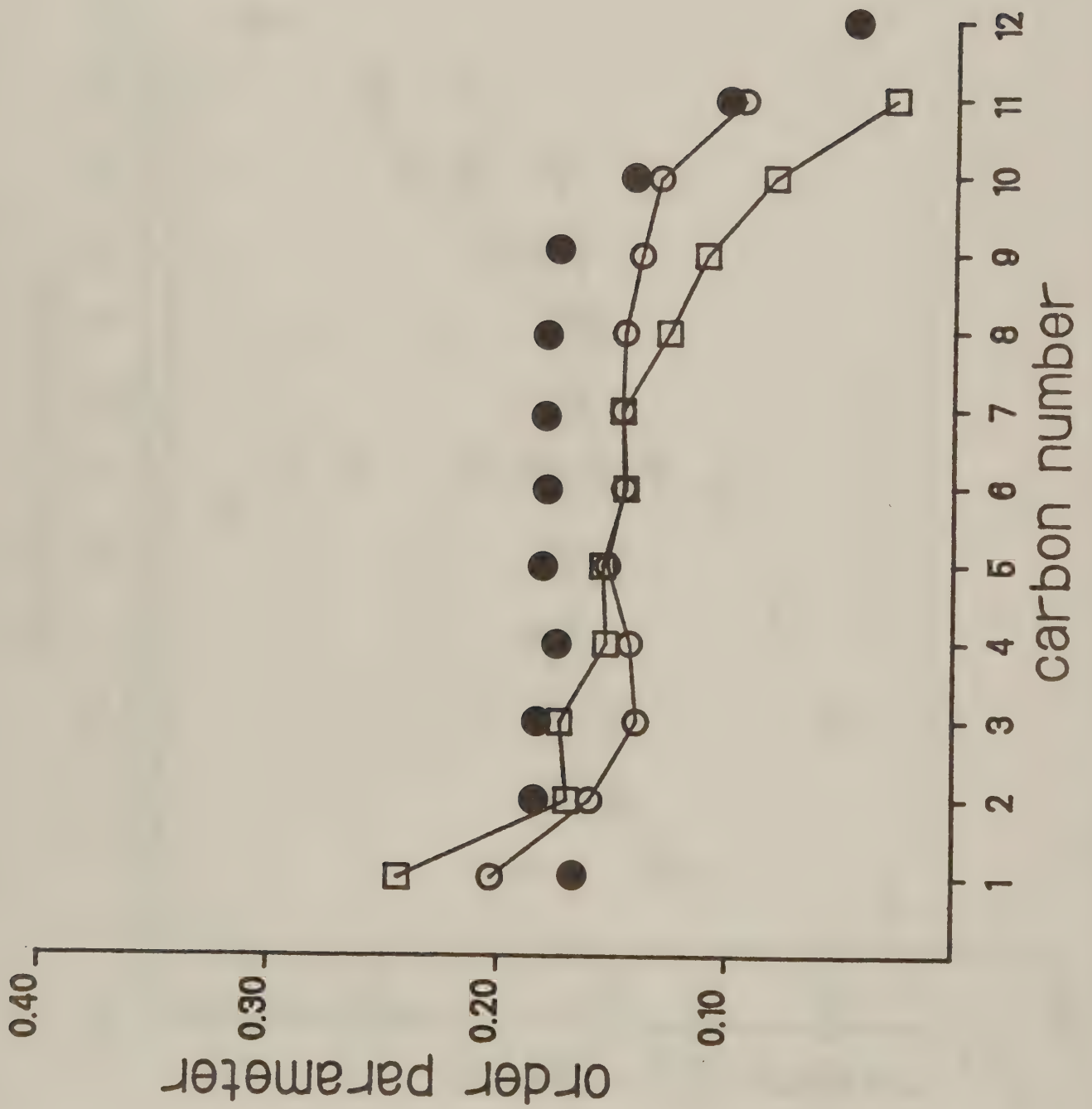


FIGURE 3 c

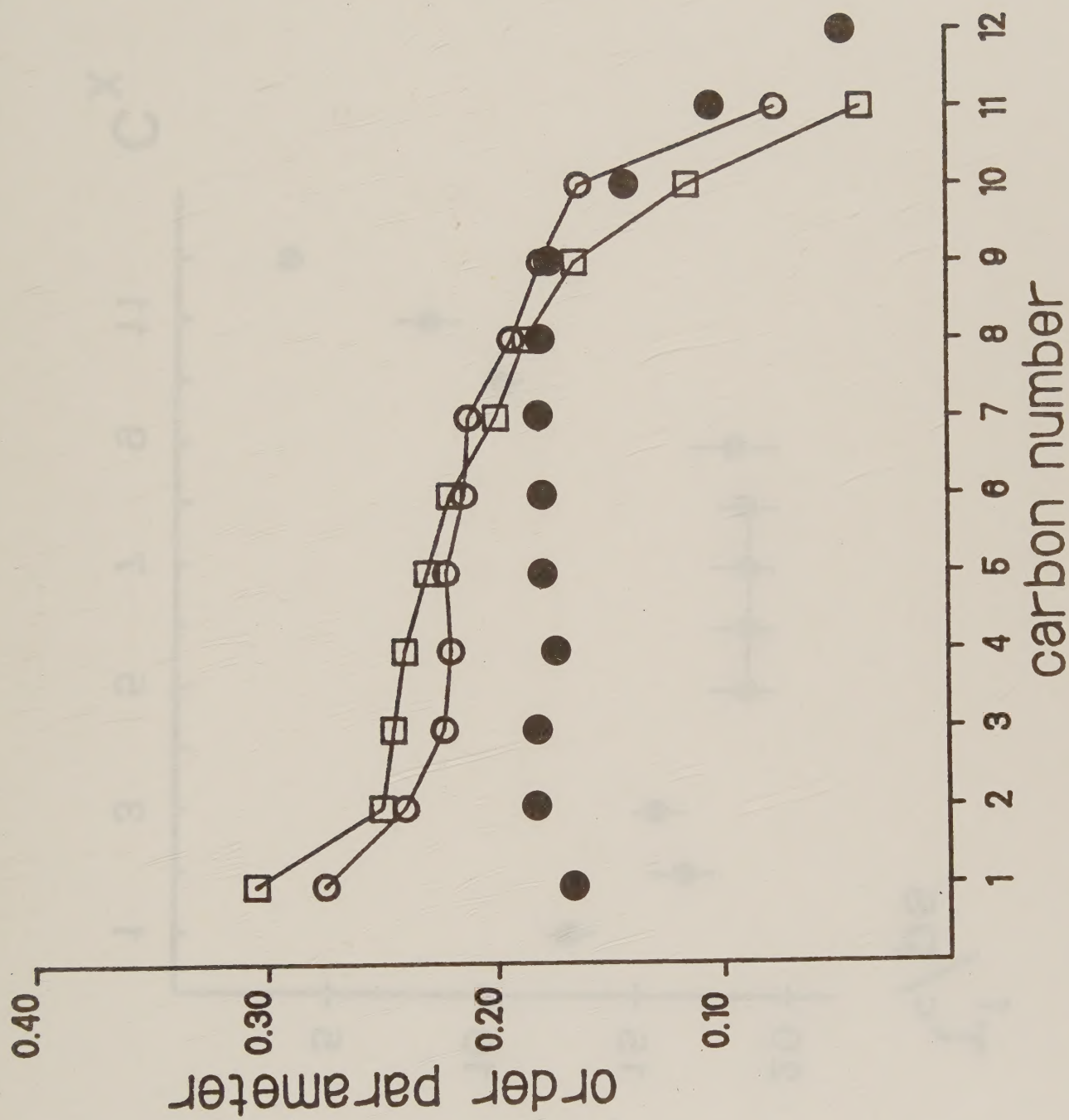


FIGURE 4

